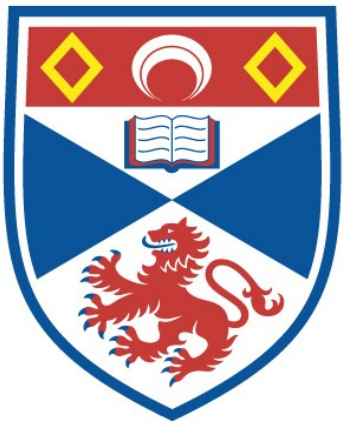
REACTIVE INTERMEDIATES IN THE REACTIONS OF ARYL HALIDES WITH STRONG BASES

Julia Kathleen Aylmer Hall

A Thesis Submitted for the Degree of PhD
at the
University of St Andrews



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REACTIVE INTERMEDIATES IN THE REACTIONS OF ARYL HALIDES WITH BASES

A Thesis
presented for the degree of
Doctor of Philosophy
in the Faculty of Science of the
University of St. Andrews
by

Julia Kathleen Aylmer Hall, B.Sc.

October 1969

United College of St. Salvator
and St. Leonard, St. Andrews.

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DECLARATION

I declare that this thesis is my own composition, that the work of which it is a record has been carried out by myself, and that it has not been submitted in any previous application for a Higher Degree.

The thesis describes results of research carried out in the Department of Chemistry, United College of St. Salvator and St. Leonard, University of St. Andrews, under the supervision of Professor J.I.G. Cadogan, since the 1st October 1966, the date of my admission as a research student.

CERTIFICATE

I hereby certify that J u l i a K a t h l e e n A y l m e r H a l l has spent twelve terms at research work under my supervision, has fulfilled the conditions of Ordinance No. 16 (St. Andrews), and is qualified to submit the accompanying thesis in application for the degree of Doctor of Philosophy.

....

Director of Research.

ACKNOWLEDGEMENTS

I should like to express my thanks to Professor J.I.G. Cadogan for suggesting the topic of research, and to Professor Cadogan and Dr. J.T. Sharp for their continued interest, advice and encouragement throughout the three years in which the work was carried out.

The advice and assistance given by many members of the teaching and technical staffs of the Department of Chemistry in the University of St. Andrews is gratefully acknowledged.

Thanks are due to the Science Research Council for the award of a Research Studentship during the period of this work.

SYMBOLS AND ABBREVIATIONS

The abbreviations that appear in this thesis are those in common usage. In addition the following symbols are used:-

J ..... spin-spin coupling constant.

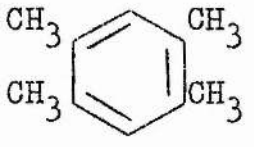
m/100m ..... moles of product per 100 moles of starting material.

M ..... molarity.

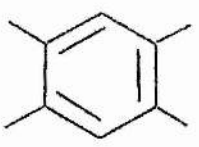
m/e ..... mass/charge ratio.

Rf ..... the ratio of distance moved by the substance to the distance moved by the solvent front.

In accord with common usage durene is represented by the formula shown below. Other methyl benzenes and derivatives are represented similarly.



is represented by



ABSTRACT

The reaction of a series of 2,6-dimethylaryl halides with strong base has been investigated. Debromination to give polymethylbenzenes has been found to occur in all the systems studied and varying amounts of higher-boiling products, mainly polymethylbibenzyls, have also been obtained. Various mechanisms for these new reactions are discussed and the participation of an unusual triplet carbene intermediate is suggested.

The related thermal decomposition of sodium o-halophenates has also been investigated. The participation of a similar carbene intermediate in this reaction appears to be unlikely. Possible mechanisms for the formation of diphenylmethanes obtained in the decomposition of sodium pentachlorophenate in methylbenzenes, are discussed.

CONTENTS

INTRODUCTION

-oOo-

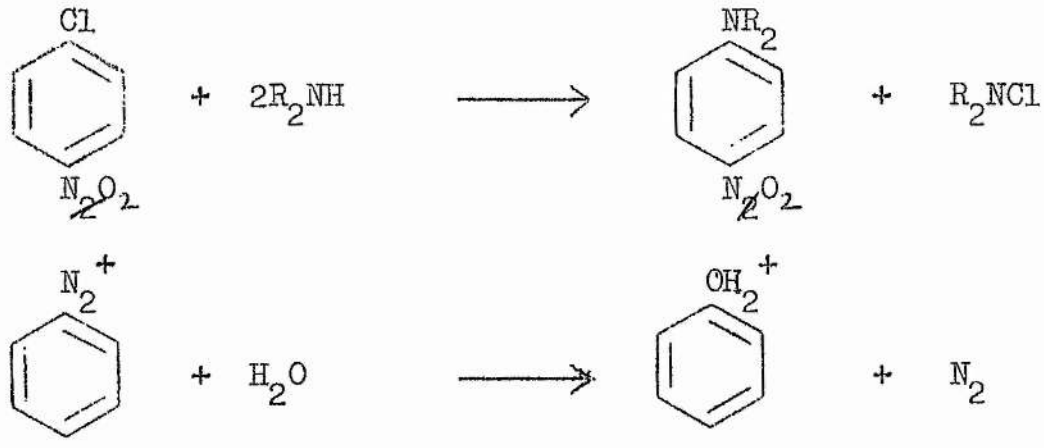
1. Preamble

The new reactions described in this thesis involve attack of strong bases on aryl halides, and decompositions of halophenols. As will be seen, some of the products of these reactions are bibenzyls reminiscent of radical derived products. Accordingly the Introduction to the thesis will deal with previously described reactions of bases with aryl halides, decompositions of halophenols and reactions of benzyl radicals.

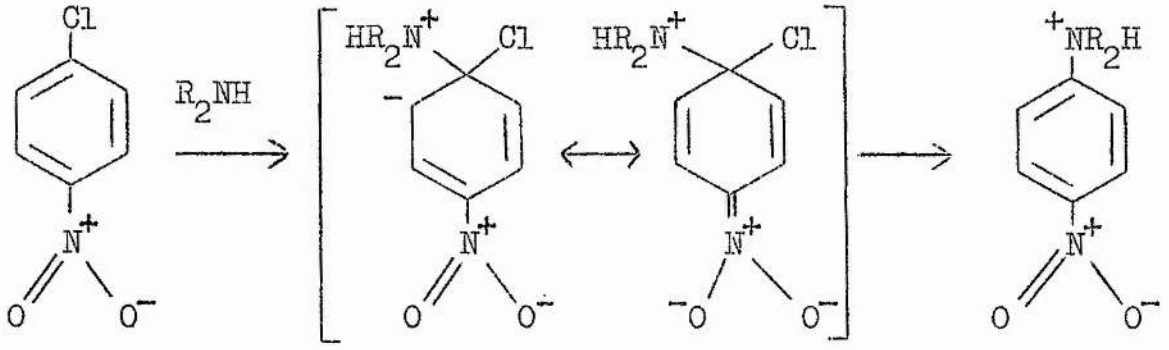
2. Reactions of Aromatic Systems with Strong Bases and Nucleophiles

Since the aromatic nucleus is a very stable system, aromatic compounds usually undergo substitutions of atoms attached to the ring, rather than reactions involving cleavage of the ring itself. Of these substitutions, the best-known are probably those involving electrophilic displacement of hydrogen, for example the familiar nitration, halogenation, and Friedel-Crafts reactions.

Organic textbooks tend to devote less space to aromatic nucleophilic substitutions. 'Normal' aromatic nucleophilic substitution, where the mechanism is similar to aliphatic nucleophilic substitution, involves displacement of an atom or group which can form a reasonably stable anion and usually requires the presence of activating substituents in the ring. Examples of reactions of this type are the amination of p-chloronitrobenzene, and the decomposition of aromatic diazonium salts.



As with aliphatic nucleophilic substitutions, two mechanisms are displayed. Thus the displacement of chlorine from p-chloronitrobenzene is a bimolecular, SN2, reaction involving an intermediate (1) stabilised by the nitro group.



(1)

On the other hand, the decomposition of benzene diazonium salts shows characteristics, such as first-order kinetics and no dependence of rate on the nature of the attacking anion, of a unimolecular, SN1, mechanism, in which the formation of the carbonium ion is the rate-determining step, i.e.:

$$ArN_2^+ \xrightarrow[\text{slow}]{-N_2} Ar^+ \xrightarrow[\text{fast}]{HOH} ArOH + H^+$$

Aromatic systems which do not contain activating groups usually require the use of very strong bases or nucleophiles, and generally forcing conditions to effect any reaction. Although

direct nucleophilic substitution does occur, more complex mechanisms, often involving several steps, are usually observed, and complex products, as well as simple substitution products, are obtained.

Early work in this field includes that of Kym,[1] who studied the preparation of N-phenylnaphthylamines from halonaphthalenes, arylamines and soda-lime at 350°, the preparation of tetraphenyl-phenylenediamines from dichlorobenzene and potassium diphenylamine by Haeussermann,[2] the alkali fusion of arene sulphonates,[3] and the alkali fusion of halogeno-phenols.[4] Many of these workers noticed that rearrangements took place during the reaction, but no attempt was made to explain the mechanism.

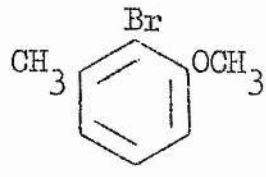
Later, reactions of this type were investigated by Bergstrom and his co-workers[5] in the reaction of aryl halides with potassium amide in liquid ammonia, by Wittig[6] in the formation of biphenyl from phenyl lithium and halobenzenes, and by Gilman[7] in his studies of metal-halogen interconversion. Subsequently the mechanism of these reactions has been studied in some detail.

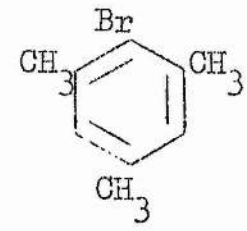
Bunnett and Zahler[8] state that the term 'aromatic nucleophilic substitution' applies only to substitutions at carbon atoms forming part of an aromatic ring, and excludes substitution reactions in side-chains of aromatic compounds. Similarly, in this survey, only those reactions which involve the breaking of bonds to the carbon atoms of the aromatic ring will be considered.

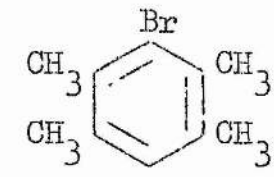
(a) Reactions involving aryne intermediates

Although the existence of aryne intermediates was only postulated about thirteen years ago, a great deal of study has been devoted to it. Among surveys in this field are those of Hoffmann,[9] Wittig,[10] Bunnett,[11] and Heaney.[12]

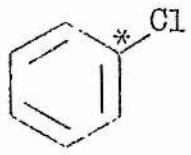
(i) Evidence for the formation of arynes: Many of the early workers mentioned above (page 4) noticed that reactions of aryl halides under forcing conditions were accompanied by rearrangements in the products. Later workers observed similar rearrangements, especially when using sodium or potassium amides in liquid ammonia and lithium dialkylamides in ether,[13] and the term 'cine-substitution' was invented[8] for them. Further information was gained when it was discovered that, when rearrangement took place, the entering group always occupied the position ortho to the leaving group and that, where the ortho positions were blocked, as in the following systems, no substitution occurred.[14,15]







Using ^{14}C labelled chlorobenzene (2) and iodobenzene (3), Roberts[15] showed that almost equal amounts of rearranged and



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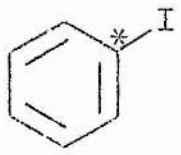
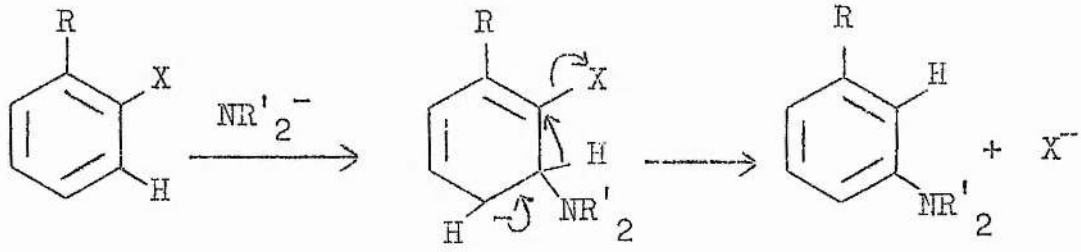


(3)

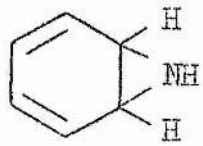
unrearranged products were formed, requiring reaction via a symmetrical intermediate. An alternative mechanism was suggested in which the products were obtained by a combination of direct displacement and isomerization[16] as shown below:



This was ruled out by the fact that chlorobenzene-1-^{14}C and iodobenzene-1-^{14}C gave the same product mixtures, although such different halogens would hardly be expected to give the same ratio of direct displacement to isomerization reactions. In addition the hydrogen-deuterium isotope effect for the amination of bromobenzene was found to be 5·5.[17] If the products were obtained by a combination of direct displacement and isomerization, this result would suggest a primary isotope effect of about 11 for the isomerization reaction, which is not in principle possible.

Roberts suggested[17] that the intermediate involved in the reaction was dehydrobenzene or benzyne (4). Other possible intermediates, (5)-(8), were ruled out as follows. Intermediates (5) and (6) were rejected because the large deuterium isotope effect

(4)



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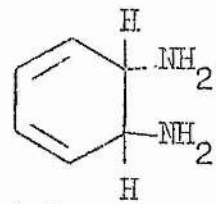

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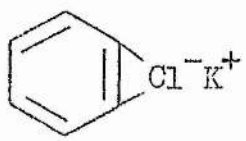

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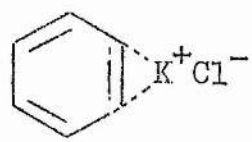
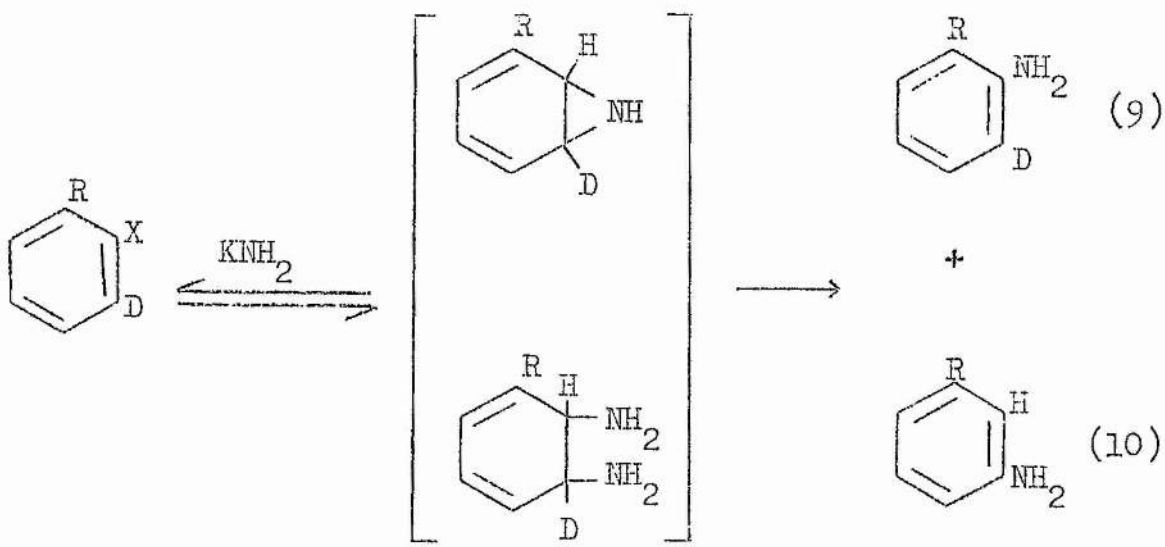
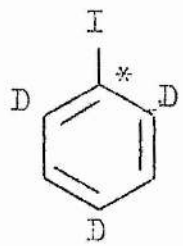


(8)

would require that the first, endothermic, step in the scheme shown be fast and reversible, with the exothermic loss of ammonia as rate-determining step.



Furthermore, because of the size of the isotope effect, more (9) should be formed than (10). This was shown[18] not to be so by using iodobenzene-1-^{14}C-2,4,6-D_3 (11).



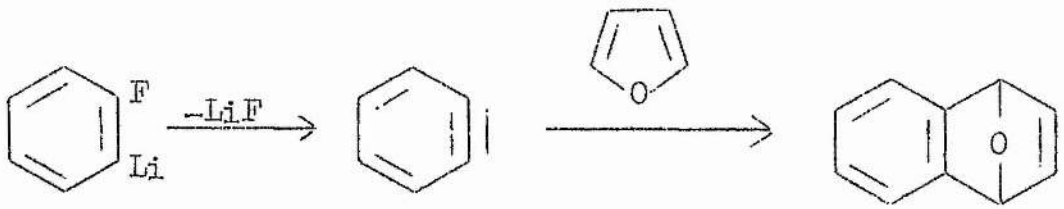
(11)

Intermediate (7) was ruled out on the grounds that aryl fluorides give the same pattern of products with lithium diethylamide in ether as the other aryl halides,[19] although fluorine would be unlikely to expand its valence shell to accommodate the ten electrons required.

This intermediate was also excluded by the observation[20] that the competition constant for the addition of lithium piperidide and phenyl lithium to benzyne, generated from various aryl halides, is independent of the nature of the halogen, although one would expect the selectivity of intermediate (7) to be affected by the halogen.

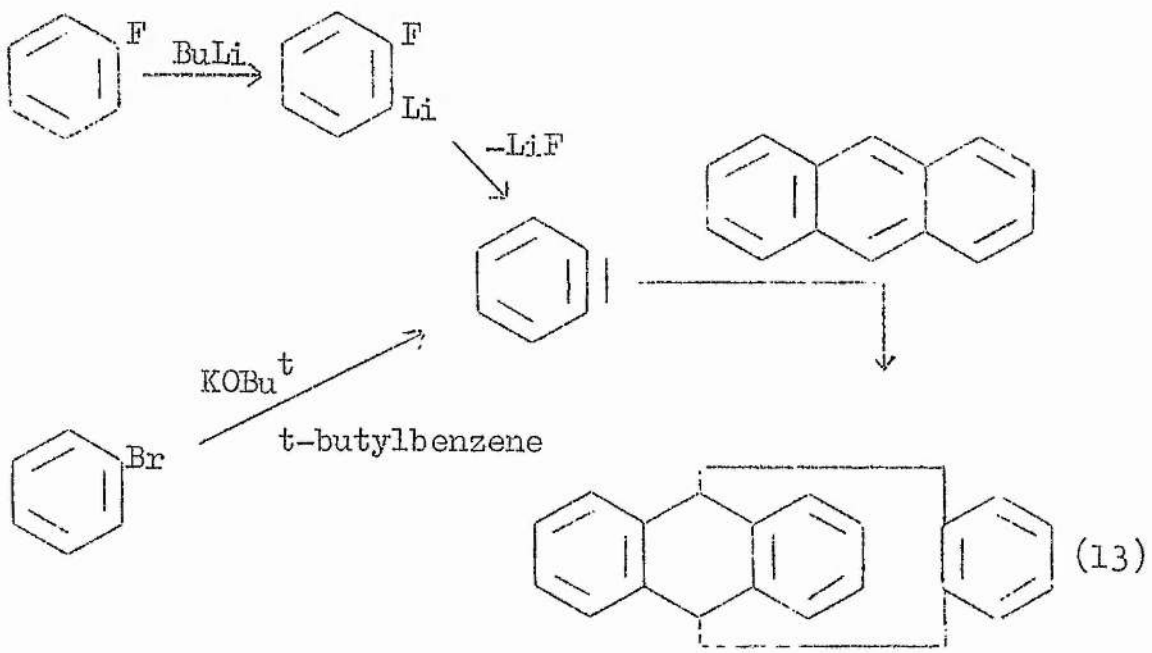
It is unlikely that an alkali metal cation would complex with an unsaturated hydrocarbon such as benzyne in the presence of much better complexing agents such as ammonia, and for this reason intermediate (8) was also excluded.

More positive evidence for the existence of benzyne can be obtained using the suggestion, made by Wittig,[21] that benzyne should react as a dienophile. By treating o-bromofluorobenzene with lithium amalgam in furan, a reaction in which benzyne was postulated as an intermediate, he obtained the endoxide (12).



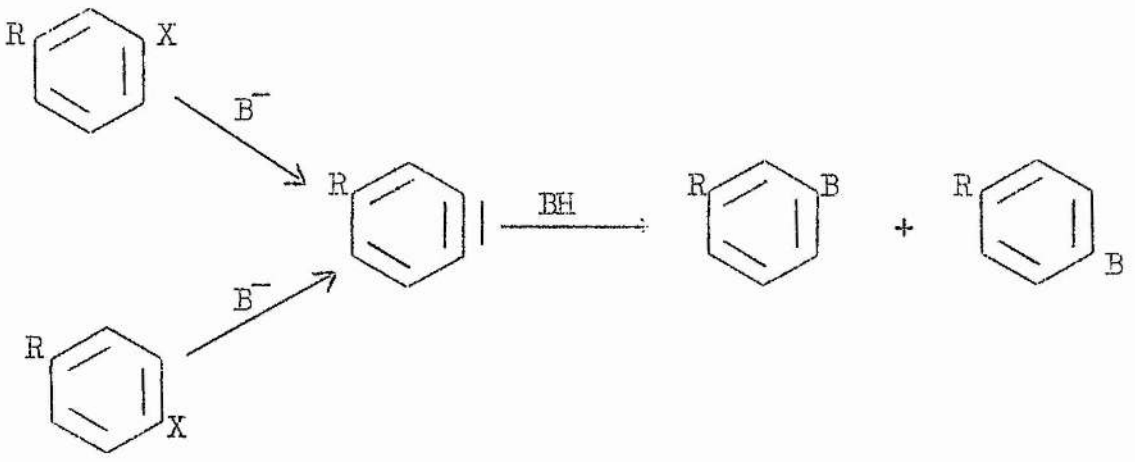
(12)

In a similar manner using anthracene as the diene, triptycene (13) can be formed. Such reactions, to give Diels-Alder adducts, are now frequently used as diagnostic tests for the presence of aryne intermediates in a reaction.[22,23]



(13)

When substituted aryl halides are used in the reaction, the intermediate formed is no longer symmetric and products should be formed in a ratio characteristic of the substituent. Although the same intermediate can be formed from different starting materials, the same ratio of products should be obtained when any one intermediate is involved.



The yields of isomers obtained from various substituted aryl halides when treated with sodamide in liquid ammonia,[24] and with potassium t-butoxide in t-butylbenzene[23] are compared in Table 1.

Similar agreement is found with other systems, for example using substituted aryl halides with phenyl lithium in ether,[25] and using substituted aryl halides with lithium piperidide in ether.[26]

It is interesting to note that, although the benzyne intermediate is too reactive to have been detected in solution except

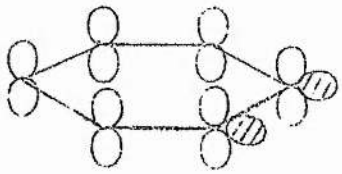
TABLE 1: Percentage of Isomers Obtained in the Reactions of Substituted Aryl Halides with Different Bases

Substituent	Base	Yield of isomers (%)		
		o	m	p
o - Me	$KOBu^t$	20	80	
	$NaNH_2$	48	52	
m - Me	$KOBu^t$	6	59	35
	$NaNH_2$	22	56	22
p - Me	$KOBu^t$		51	49
	$NaNH_2$		60	40
o - MeO	$KOBu^t$	3	97	
	$NaNH_2$	0	100	
m - MeO	$KOBu^t$	3	97	
	$NaNH_2$	0	100	
p - MeO	$KOBu^t$		48	52
	$NaNH_2$		49	51
o - CF_3	$KOBu^t$	2	98	
	$NaNH_2$	0	100	
m - CF_3	$KOBu^t$	1.5	93	5.5
	$NaNH_2$	0	100	
p - CF_3	$KOBu^t$		47	53
	$NaNH_2$		50	50

by indirect evidence, as in the formation of adducts, it has been detected by physical methods in the gas phase. Berry and his co-workers[27] have observed signals in mass and ultra-violet spectra recorded during photolysis of benzene diazonium o-carboxylate, which they attribute to benzyne. 1,3-Dehydrobenzene, and 1,4-dehydrobenzene have been observed[28] using similar techniques.

(ii) Structure of benzyne: It can be imagined that benzyne is formed from benzene by removal of two hydrogen atoms from adjacent

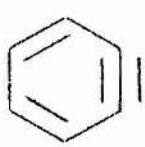
carbon atoms, leaving two electrons in sp^2 orbitals orthogonal to the π electron system, as shown in (14).

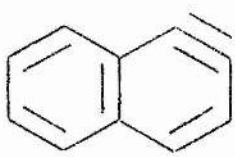


(14)

These two sp^2 orbitals can interact to give either a singlet, spin-paired, or a triplet, spin parallel, state. Since free-radical reactions of benzyne are not common and since those that do occur can be explained without treating benzyne as a diradical, the triplet structure seems unlikely. If benzyne does exist in a singlet state then a bond is formed, and some overlap of the sp^2 orbitals should occur.[9]

The increased stability of 9,10-dehydrophenanthrene (15) and 1,2-dehydronaphthalene[20] (16) can be attributed to the increase in overlap which is possible where the bond-length is shorter.





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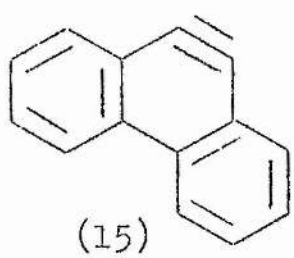
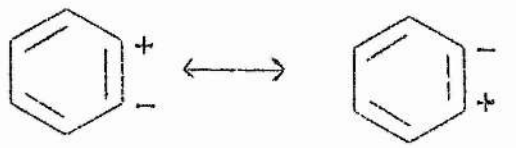


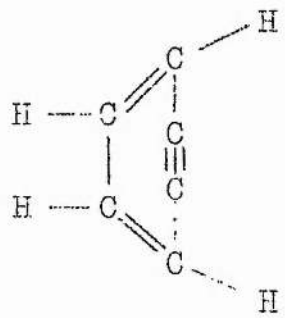
(15)

A dipolar structure (17) for benzyne is unlikely in the ground state since there is evidence[9] that it does not react as a dipole.



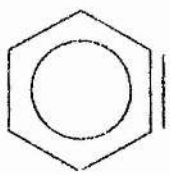
(17)

A linear acetylenic bond is ruled out by the geometry of the six-membered ring required to accommodate it, and although bent forms of acetylene are known, these are excited states of much higher energy than benzyne.[9]



(18)

It can therefore be assumed that benzyne involves the formation of some form of weak bond between two adjacent sp^2 orbitals. This situation is perhaps best represented by formula (19)[9] although (20) is very commonly used. It should be remembered, however, that



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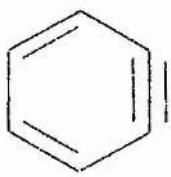

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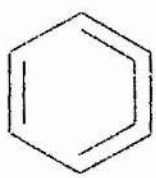
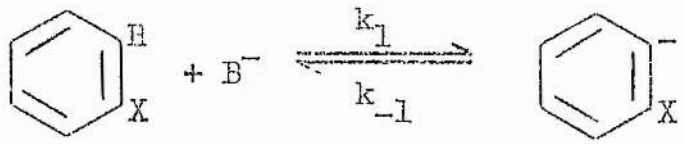


(21)

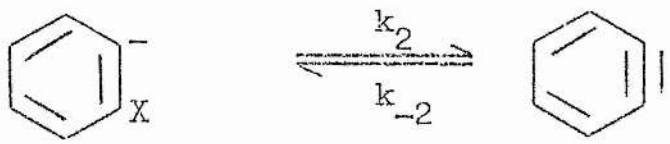
the triple bond in formula (20) is formal only; recent molecular-orbital calculations[29] suggest considerable contribution from

structures similar to (21).

(iii) Scope and mechanism of benzyne formation: The complete equation for the formation of benzyne from aromatic compounds is represented below. The effects of variations of solvent, B^- and X, on the rates k_1, k_{-1}, k_2, k_{-2} have been extensively studied.



(i)



(ii)

A wide variety of reagents has been used to generate the anion in step (i) of this reaction scheme. Organo-metallic compounds are the most efficient[9] and are often used, particularly lithium alkyls such as phenyl lithium and t-butyl lithium. Alkali metal amides are also frequently employed, both in protic[5,15,17] and aprotic[20,21b] solvents.

Weaker bases, such as potassium t-butoxide[23,30] and other alkoxides and hydroxides require more forcing conditions.

The effect of solvent on metallation can be quite marked.

In protic solvents, such as liquid ammonia, fluorobenzene is not aminated[17] by sodamide, and chlorobenzene reacts more slowly than bromobenzene or iodobenzene. The overall order of reactivity is Br > I > Cl > F. In ether, however, fluorobenzene reacts more rapidly than the other halobenzenes, the order of reactivity being F > Cl > Br > I.

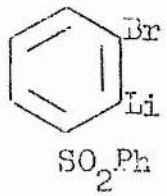
Roberts explained[17] this phenomenon by invoking two alternative mechanisms. This is unnecessary, however, since the reactivities can be explained more simply[9] as follows. The sequence F > Cl > Br > I is the order of reactivity for the metallation of aryl halides, and is to be expected if k_1 is rate-determining. This is the sequence found in aprotic solvents. In protic solvents step (i) of the scheme on page 14 becomes reversible and again the order of reactivity to reprotonation is F > Cl > Br > I. Thus in protic solvents fluorobenzenes are reprotonated before they can decompose to benzynes. Under these circumstances k_2 may become rate-determining, in which case the order of reactivity I > Br > Cl > F operates. Superimposition of these two sequences leads to the order of reactivity observed in protic solvents, i.e. Br > I > Cl >>> F. In fact the order of reactivity depends on the term $k_{-1}[BH]$, so that changes in the concentration of base can be used to vary the reactivity of the various aryl halides.

The effect on reactivity of varying the halogen, X, is

discussed above. The influence of X on the metallation step (i) is due to its inductive effect which affects the acidity of the ortho hydrogen atoms. The effect of X on step (ii) of the mechanism is only of importance if step (i) is reversible and therefore not rate-determining. The thermal stability[31] of the anions gives a measure of the leaving ability of the various halogens. Although other leaving groups can be used, these lie outside the scope of this discussion.

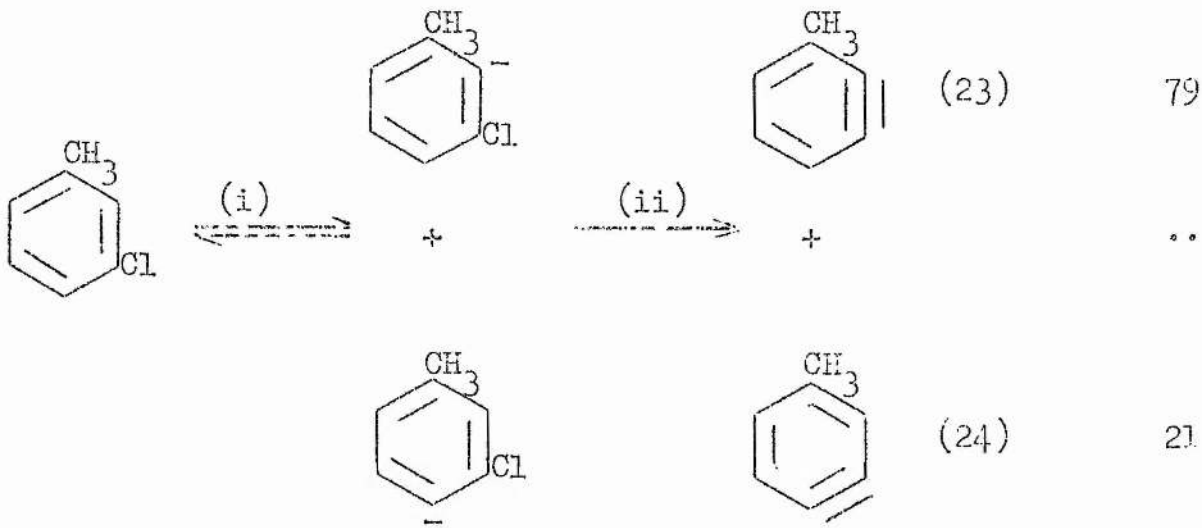
Substituents in the benzene ring will affect both the metallation step and the formation of benzyne. Electron-donating groups decrease the acidity of the proton in the ring, thus retarding metallation, while electron-withdrawing groups have the reverse effect. However, since metallation involves σ-bonds, rather than the aromatic π-electron system, inductive effects are of primary importance, while mesomeric effects probably influence only the ease of approach of the metallating agent.[9]

Similarly inductive effects operate during step (ii), the formation of benzyne. Electron-withdrawing groups stabilise the negative charge on the anion, thus strengthening the C-X bond and inhibiting loss of X, while electron-donating groups tend to destabilise the anion. So great is the inductive effect of the benzene sulphonyl group that (22) has a considerable lifetime at room temperature.[32]



(22)

Amination of 3-chlorotoluene with potassium amide in liquid ammonia shows [33] the ratio of formation of the two possible benzynes (23) : (24) to be 79 : 21. The ratio for 3-bromotoluene is 40 : 60 and since, in this case, metallation is not reversible this gives the ratio of formation of the two anions. Since metallation is



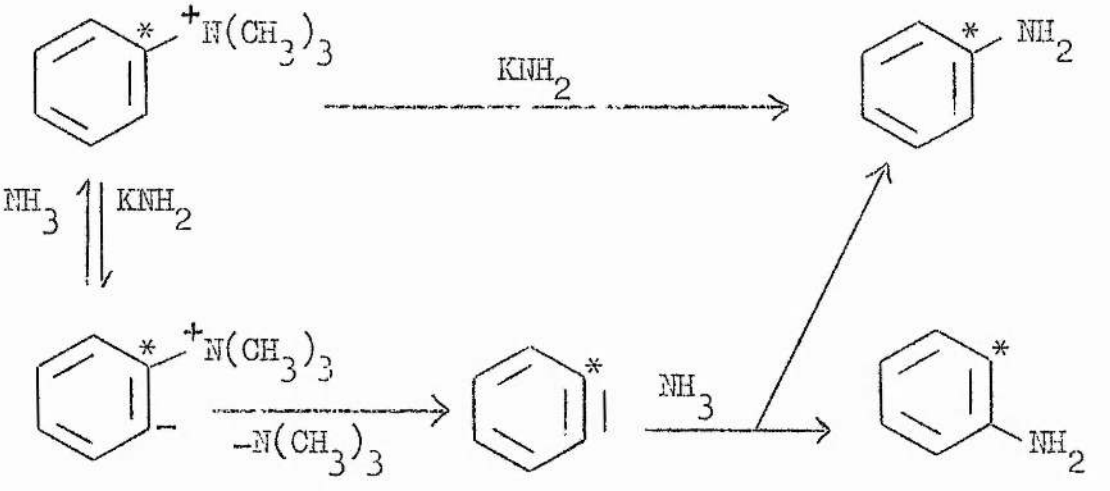
reversible for chlorotoluene, the greater proportion of (23) formed shows that it is formed more readily in step (ii) than (24). This is a result of the inductive effect of the methyl group.

Reactions of aryl halides with strong base involving benzynes have been studied extensively, because of the interest of the

benzyne intermediate itself, both mechanistically and for synthesis. Other mechanisms for reaction between aryl halides and strong base have received less attention up till now.

(b) Reaction via direct nucleophilic substitution

It was mentioned above (page 16) that groups other than halogen could act as the leaving-group in the formation of arynes. In the reaction of N-trimethylanilinium ions with potassium amide in liquid ammonia, about 4% of the aniline formed is found to be rearranged, indicating participation by benzyne. The major part of the aniline formed, however, is due to direct nucleophilic substitution.[17]



This competition between the benzyne, elimination-addition, mechanism, and direct nucleophilic substitution is observed in other cases, especially where weaker bases are used. It is shown,

for example, in the reaction of bromonaphthalene with piperidine and sodamide.[34] In piperidine alone, bromonaphthalene reacts, at 230°, exclusively by direct substitution. If sodium amide is present, thus increasing the basicity, reaction occurs at 100° via the naphthalyne intermediate.

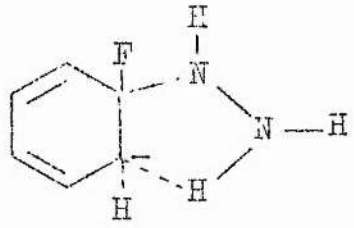
In the hydrolysis of aryl halides to phenols using aqueous sodium hydroxide,[35] hydrolysis of chlorobenzene-1-^{14}C at 340° with 4M sodium hydroxide gave 58% phenol-1-^{14}C and 42% phenol-2-^{14}C. The benzyne mechanism should give an equimolar mixture of products, so this result suggests that some phenol-1-^{14}C is formed by direct nucleophilic substitution. At 250° the effect is more marked. Chloro-, bromo-, and iodotoluenes should give the same ratio of rearranged to unrearranged product if only the benzyne mechanism operates. Roberts[35] found that more unrearranged product was formed, in all cases, than was obtained with the corresponding chlorotoluenes at 340°. The susceptibility to direct substitution was I > Br > Cl, which is to be expected from a consideration of the stability of the anions formed.

In contrast, however, it is reported[36] that aryl halides react with methanolic sodium methoxide solely by direct substitution, and that fluorobenzene reacts up to 100 times faster than chlorobenzene. This order of reactivity is also found[8] in activated nucleophilic substitution. Again, fluorine is found to be far more

susceptible than the other halogens to direct nucleophilic substitution in reactions of halonaphthalenes with sodium amide in piperidine, where 1-fluoronaphthalene reacts substantially by direct substitution,[37] and in reactions of aryl halides with potassium t-butoxide in dimethyl sulphoxide.[30]

This change in the order of reactivity can be attributed to a change in the rate-determining step in the addition-elimination mechanism of direct substitution.[9]

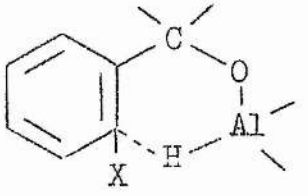
Another case involving direct displacement is the reaction of fluorobenzene with sodium hydrazide.[38] Here the ease of the substitution mechanism is attributed to the formation of the intermediate (25). Sodium N,N-dimethylhydrazide, which cannot form a similar intermediate, reacts only via benzyne.



(25)

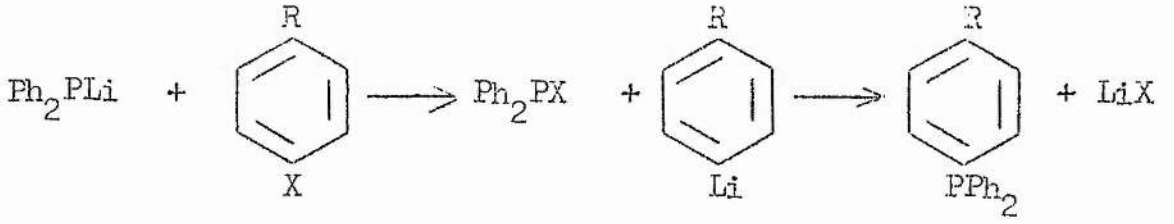
Cyclic transition states are claimed to facilitate direct nucleophilic substitutions in other systems. For example, the reduction of aryl halides with lithium aluminium hydride is shown[39] to be a direct displacement by hydride ion, at any rate in the case of 1-bromo-8-hydroxynaphthalene : by the use of lithium aluminium

deuteride. The intermediate (26) is postulated to explain the greater reactivity of aryl halides having groups capable of forming alkoxides with lithium aluminium hydride, ortho to the halogen.



(26)

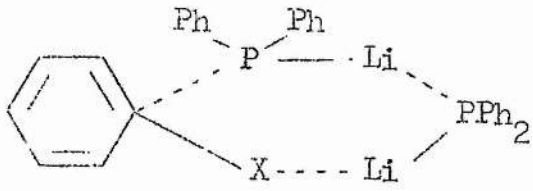
A cyclic intermediate is also proposed[40] in the reaction of lithium diphenylphosphide with aryl halides. This reaction does not take place via a benzyne intermediate since no rearranged product is obtained. The possibility of reaction by lithium-halogen interconversion can be rejected on the grounds that it should lead to the formation of tetraphenylbiphosphine, which is not observed.



$$Ph_2PX + Ph_2PLi \longrightarrow (Ph_2P)_2 + LiX$$

It can be concluded, therefore, that the reaction involves direct displacement of halogen. The fact that dropwise addition of phosphide to the aryl halide gave very much lower yields of the

diphenylarylphosphines than were obtained by addition of aryl halide to a solution of the phosphide, was used as evidence for a cyclic intermediate (27) involving two molecules of phosphide.



(27)

Other groups besides halogen may be replaced in reactions of this type. For example the alkali fusion of aryl sulphonates to give phenols has been known for many years.[3] Rearrangements have sometimes been reported, but recent work[41] has shown that only straightforward substitution products are obtained. Use of isotopic tracers confirms[42] that the mechanism is a direct nucleophilic substitution.

The foregoing examples show that direct nucleophilic substitution does occur in non-activated aromatic systems, frequently in competition with benzyne formation. It may predominate when weak bases are used in the reaction, especially if the transition state can be stabilised, for example by the formation of cyclic intermediates.

(c) Metal-halogen interconversion reactions

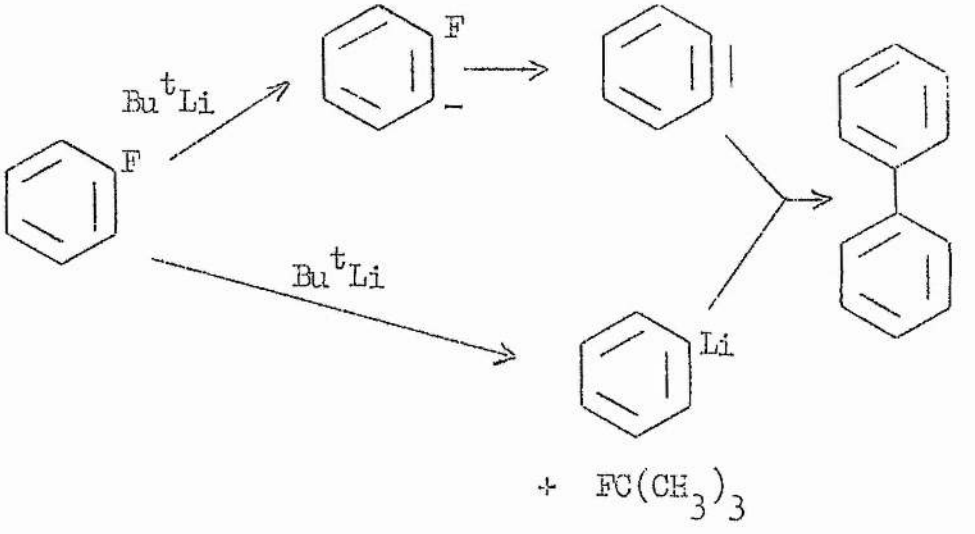
Metal-halogen interconversion reactions were studied by Gilman[7] before the detailed investigation of the benzyne mechanism. In this reaction an aryl halide and an organometallic compound exchange metal and halogen atoms:

$$RM + ArX \longrightarrow ArM + RX$$

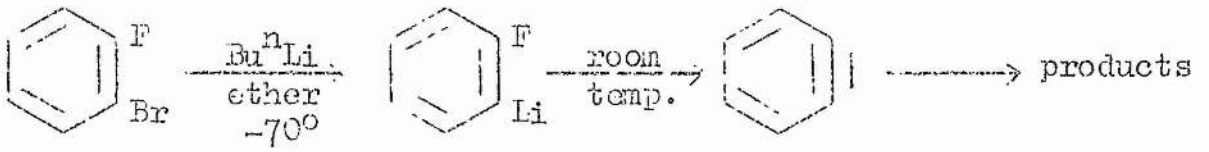
Lithium is most commonly used as the metal in these reactions, although sodium, magnesium, and even barium and aluminium can be used. The reaction is frequently used to prepare organo-lithium compounds which cannot be prepared satisfactorily by reaction of the halide with lithium itself. Bromides and iodides are found to be most susceptible to this type of reaction, chlorides less so, while fluorides react in this way very seldom. The mechanism is thought to involve removal of a positive halogen atom, by nucleophilic attack of the anion of the organo-metallic compound.[43] The organo-metallic compounds so formed will react with a wide variety of compounds, carbon dioxide, water, ketones, etc., and are very valuable in synthesis.

Reactions of this type are occasionally observed in competition with benzyne formation, especially when bromides and iodides are involved. For example, in the reaction of haloanisoles with

phenyl lithium,[44] iodoanisoles give lithium anisoles, in contrast to chloroanisoles which react via the benzyne mechanism. Even fluorobenzene is thought to undergo metal-halogen interconversion in reaction with t-butyl lithium,[45] since a small amount of biphenyl is obtained, arising from reaction of phenyl lithium with benzyne.

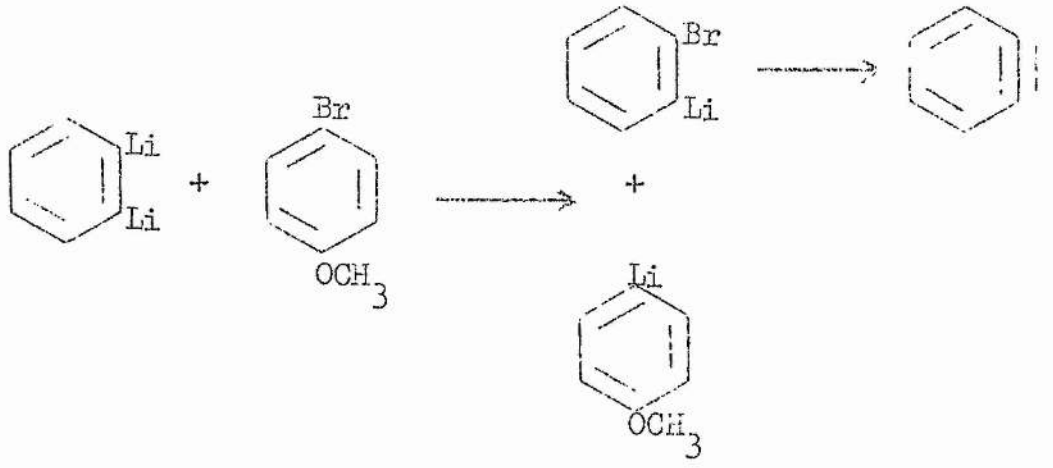


With polyhaloarenes it is possible to replace both halogens by lithium, but o-dihaloarenes were found[43] to behave anomalously. Although one halogen could be replaced rapidly, the product reacted before a second metal atom could be introduced. This behaviour can easily be explained, since the product of the replacement of one halogen is an o-halogenophenyl anion, which will decompose to benzyne. This reaction has been used[31] to generate benzyne, frequently with n-butyl lithium as the organo-metallic compound, from 1,2-halobromoaromatic compounds. When the second halogen is



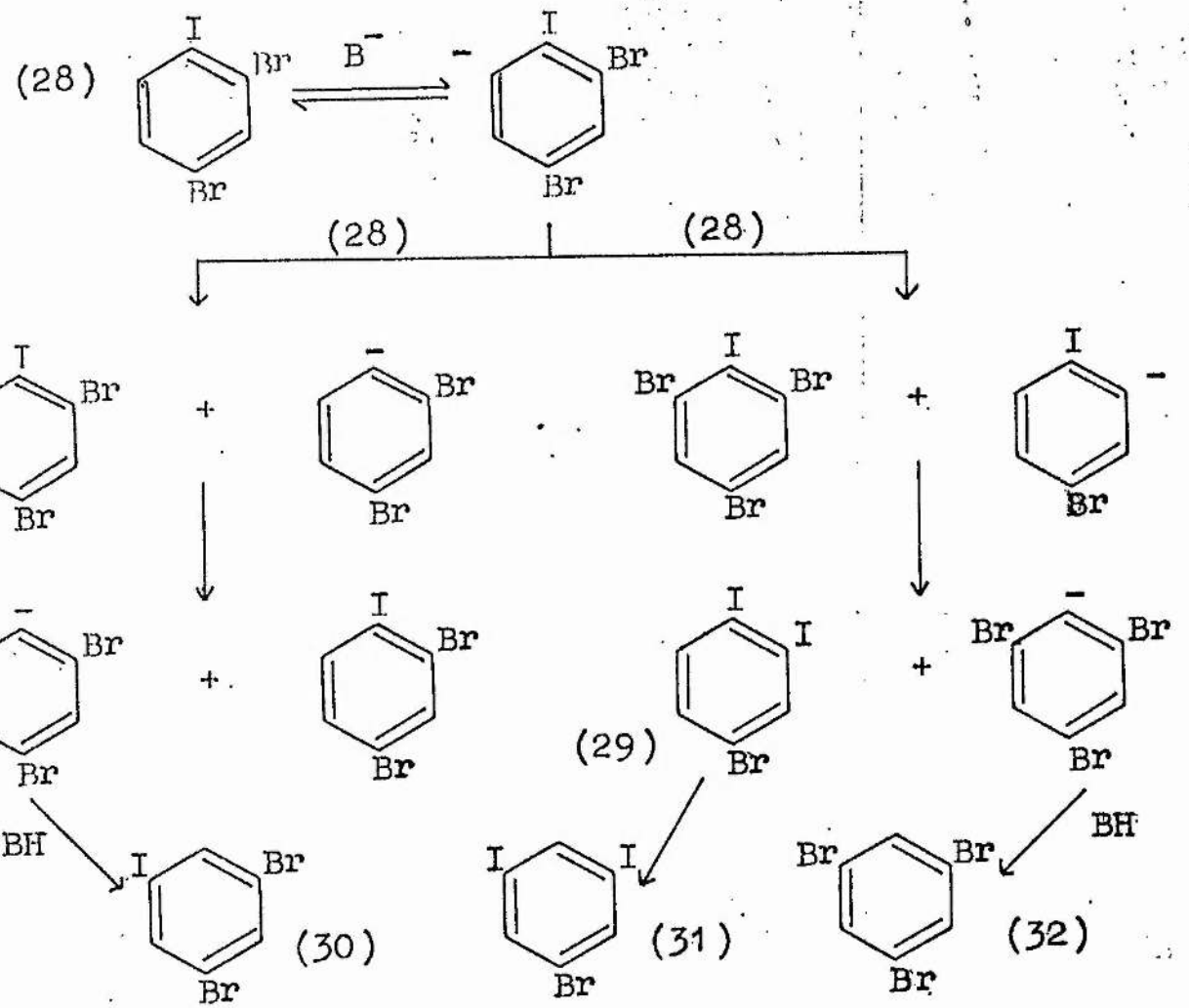
fluorine or chlorine, the more electro-positive bromine is removed; o-dibromoarenes are more reactive.[46]

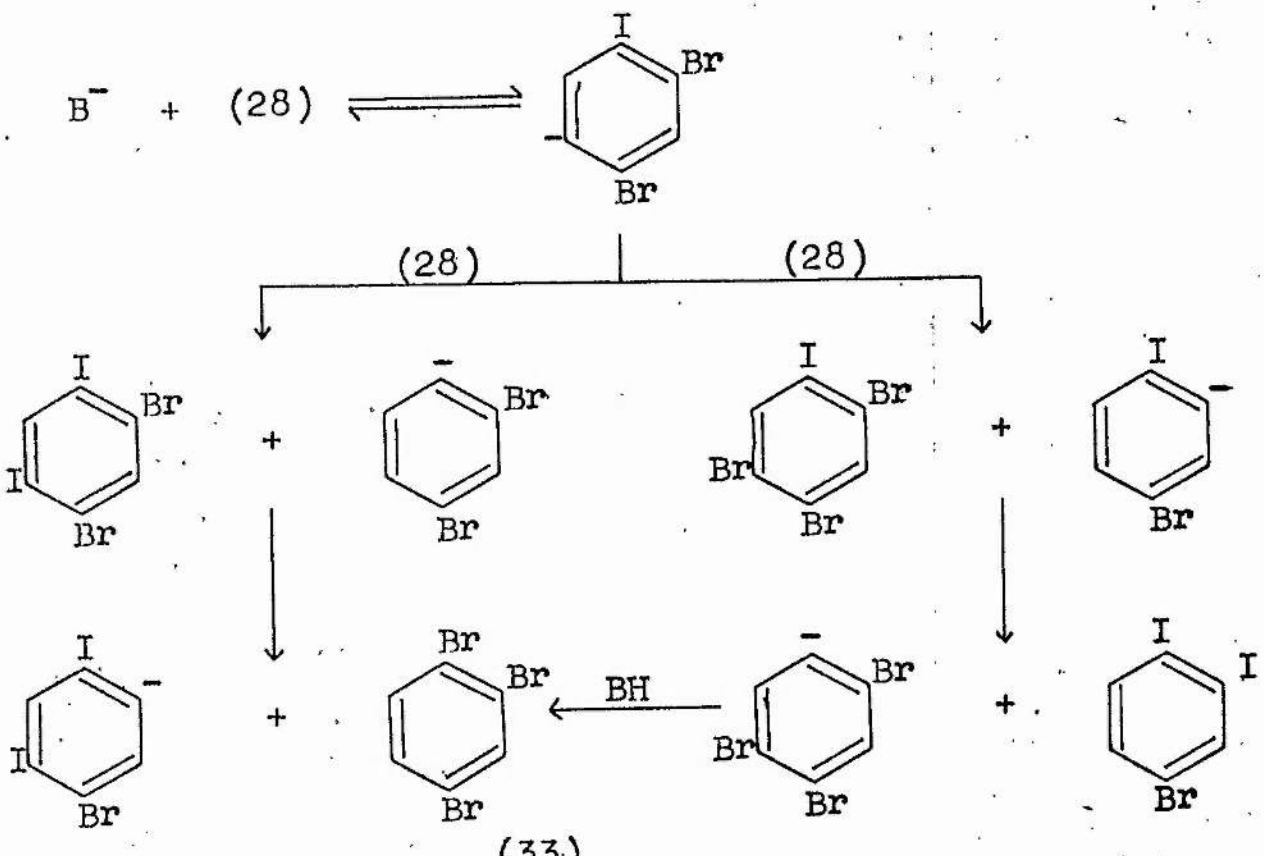
It is also possible to prepare[47] the o-halogenophenyl anion by metal-halogen interconversion starting from 1,2-dilithiobenzene which can be prepared from o-dibromobenzene via o-phenylenemercury.



It is, however, more useful to prepare benzyne from o-dihalobenzenes by metal-halogen exchange using lithium amalgam or similar reagents, since this avoids the use of strong bases and enables the reactions of benzyne with reagents other than nucleophiles, to be studied.

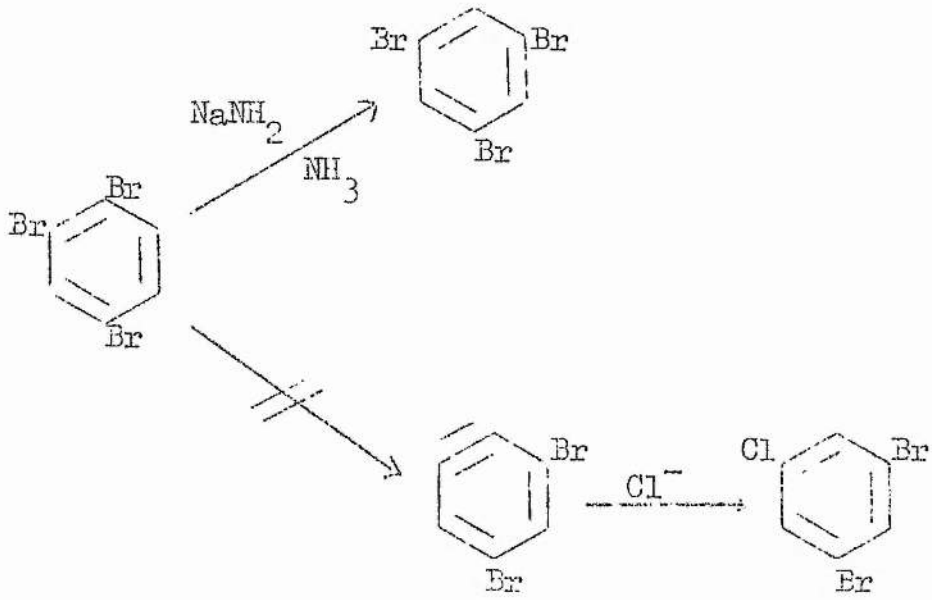
Recently nucleophilic attack on halogen has been used to


(28)
B⁻
(28)
(28)
(29)
BH
(30)
(31)
(32)
BH


B⁻ + (28)
(28)
(28)
BH
(33)

explain the mechanism of reactions involving isomerization, and reduction, of trihalobenzenes with strong bases, and as an alternative to the benzyne mechanism for cine-substitution.

1,2,4-Tribromobenzene is isomerized to 1,3,5-tribromobenzene by sodamide in liquid ammonia.[48] Investigating this reaction, Bunnett and Moyer[49] found that addition of potassium chloride or iodide did not give dibromochlorobenzene or dibromoiodobenzene, which might be expected if benzyne were an intermediate.



Reaction with 1-iodo-2,4-dibromobenzene (28) gave 1-iodo-3,5-dibromobenzene (30) and 1,2,4-tribromobenzene (33) as major products, with a little 1-bromo-3,5-diiodobenzene (31) and a trace of 1,3,5-tribromobenzene (32). The mechanism was thought to involve a series of nucleophilic attacks on halogen atoms by phenyl anions, as shown opposite. (31) would arise from a similar series of

steps on the product (29). Since the anions formed in this reaction are o-halogenophenyl anions, it should be possible for decomposition to benzyne intermediates to occur, although the anions are stabilised by the withdrawing effect of the halogen, and in fact it was found to be the major reaction path when excess base was used.

Nucleophilic attack on halogen is also suggested[50] in the mechanism of the reduction of 1,2,4-tribromobenzene, and a number of other polyhalobenzenes with potassium t-butoxide in a t-butanol dimethyl sulphoxide (1:1) mixture. In this case the attacking nucleophile is thought to be the methanesulphinyl anion (34).

$$t\text{-}BuO^- + CH_3SOCH_3 \rightleftharpoons t\text{-}BuOH + CH_3SOCH_2^- \quad (34)$$

$$CH_3SOCH_2^- + ArX \longrightarrow Ar^- + CH_3SOCH_2X$$

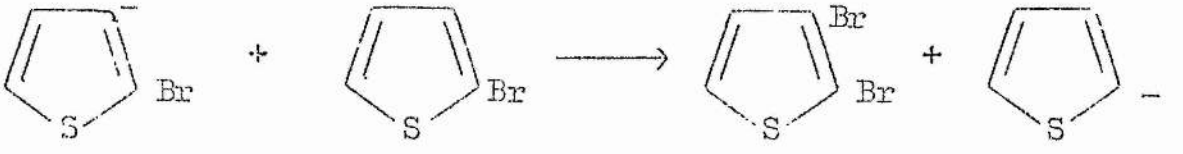
$$Ar^- + t\text{-}BuOH \longrightarrow ArH + t\text{-}BuO^-$$

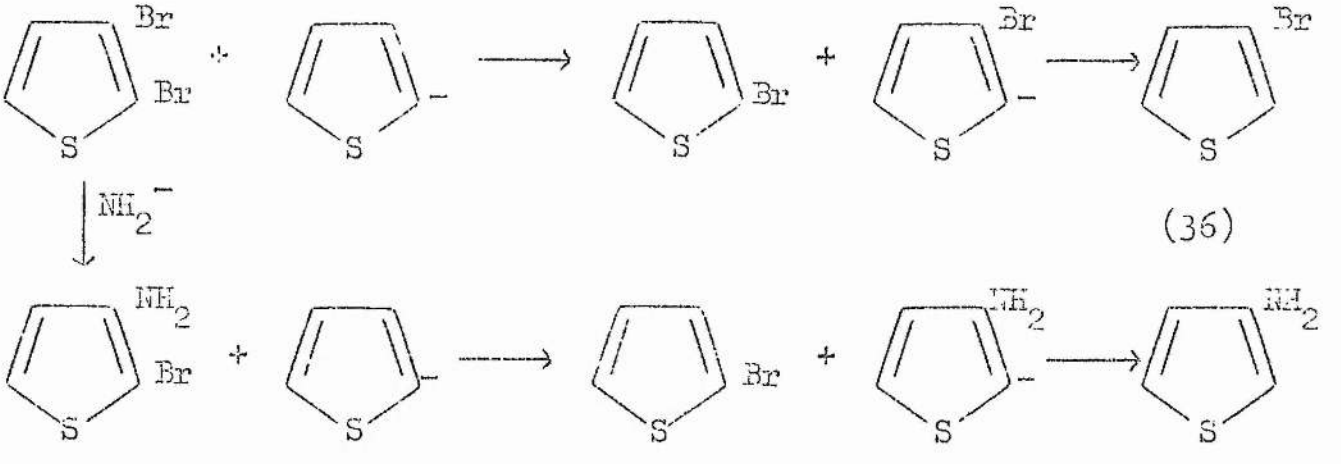
Dehalogenation also takes place in mixtures of t-butanol with other solvents, for example N-methylpyrrolidone and N,N-dimethylacetamide, in place of dimethyl sulphoxide.

Treatment of 2-bromothiophene (35) with potassium amide in liquid ammonia gives[51] mostly 3-aminothiophene (37) with a small amount of 3-bromothiophene (36). Addition of sodium bromide leads to an increased yield of 3-bromothiophene, suggesting a benzyne-like intermediate. However, addition of sodium chloride or iodide also leads to an increased yield of

3-bromothiophene with no chloro- or iodothiophenes while addition of potassium halides has no appreciable effect on the product distribution. Again the suggested mechanism involves nucleophilic attack by carbanions on bromine atoms.

(35)





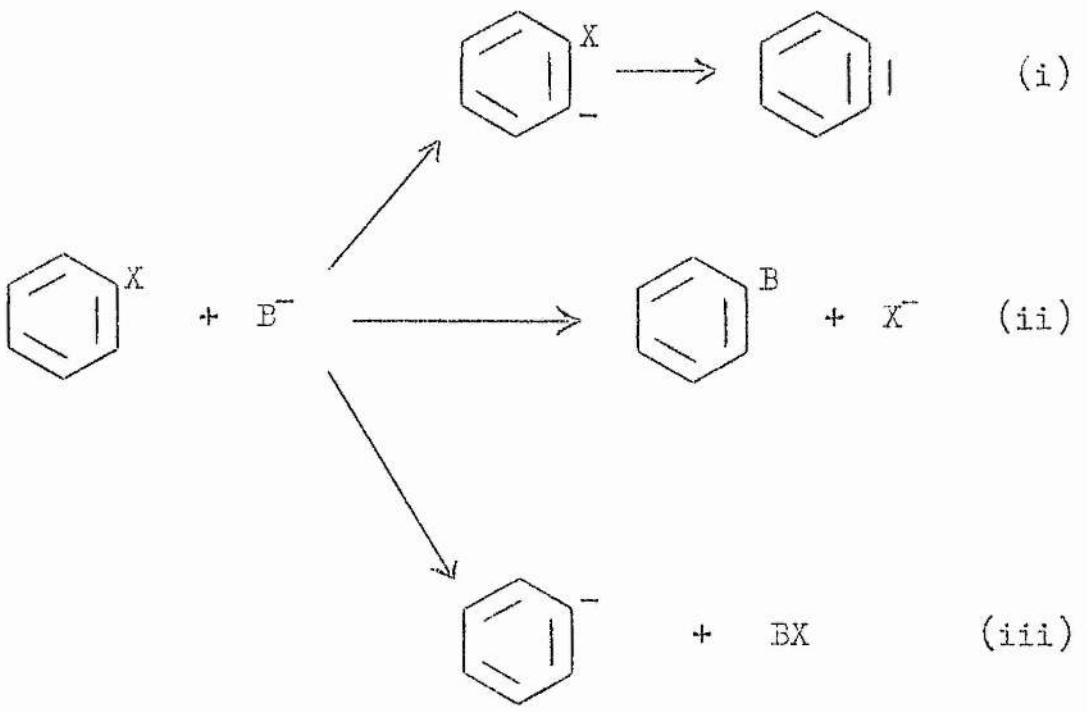
(36)

(37)

The effect of the sodium halides is explained as due to lowering of the amide ion concentration by precipitation of sodamide, which is less soluble than potassium amide.

Thus, as well as competing with benzyne formation in the reactions of aryl halides with strong base, metal-halogen interconversion can provide an alternative mechanism leading to cine-substitution.

To sum up, reactions of aromatic compounds with strong base proceed either (i) by attack on hydrogen ortho to a substituent, usually halogen, which is then lost, as an anion, to give benzyne, or (ii) by direct substitution of the substituent, or (iii) by nucleophilic removal of the substituent to give a carbanion.



Of these three, (i) is perhaps the most important and has certainly attracted the most attention; (ii) and (iii) are frequently accompanied by (i) as an alternative reaction path. It is interesting

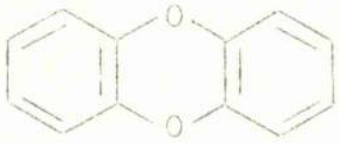
to note that the isomerization of polyhalobenzenes mentioned on page 26 involves both attack on hydrogen ortho to the halogen, and nucleophilic attack on halogen.

3. The Thermal Decompositions of o-Halophenols and their Salts

The thermal decomposition of alkali metal salts of o-halophenols can be regarded as another example of reaction between an aromatic compound and a nucleophile, in which the phenoxy anion acts as both the aromatic compound and the nucleophile.

The reactions described in the previous section were investigated in detail in order to explain the mechanism of the reaction. Perhaps because of the biological interest of the halophenols and of some of the decomposition products, these decompositions have mainly been studied in connection with their synthetic possibilities.

The thermal decomposition of the salt of an o-halophenol was first reported by Merz and Weith [52] in 1872. They heated the potassium salt of pentachlorophenol at 300° and obtained a white crystalline compound which they called 'perchlorophenyleneoxide'. In 1909 the thermal decomposition of alkali salts of o-chlorophenol was reported [53] to give diphenylene dioxide (38). More recently Tomita and his co-workers [54] have reported the preparation of

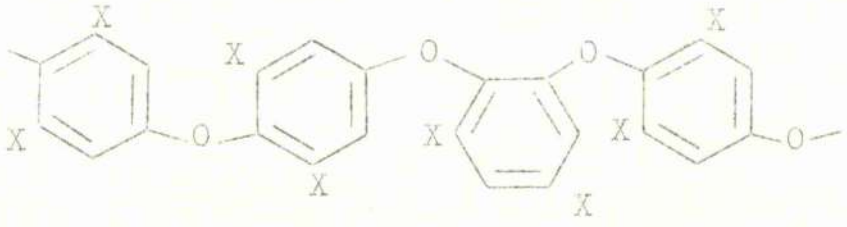


(38)

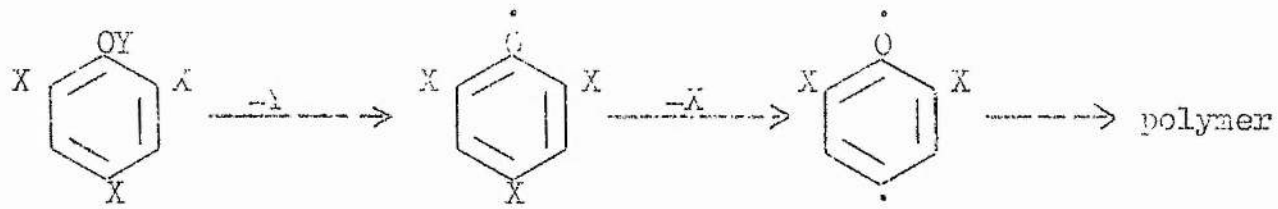
diphenylene dioxide and halogenated derivatives, by heating o-halophenols at 300°.

The decomposition of the silver salts of 2,4,6-trihalophenols in benzene at 60° was investigated by Hunter.[55] The product from this reaction obtained in good yield was a polymeric substance with the general formula $(C_6H_2X_2O)_n$ which he called poly-dihalophenylene oxide. Similar products were obtained by the action of ethyl iodide on the silver salts, and by the action of calalytic amounts of iodine on the alkali salts of trihalophenols.

Hunter was able to show,[56] using phenol salts such as silver 2,6-dichloro-4-bromophenate, that the halogen was removed from both the ortho and para positions, and that iodine was removed more easily than bromine which in turn was removed more easily than chlorine. He suggested[57] that the polymeric material consisted of halogenated benzene rings joined by ether linkages thus:

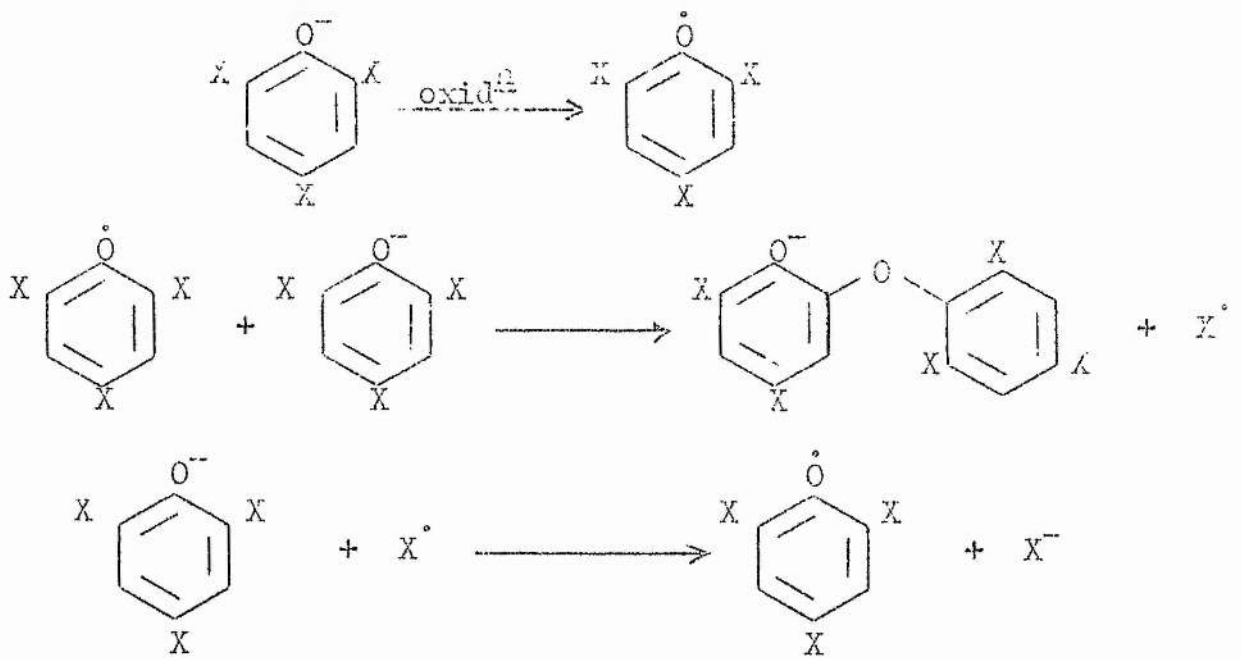


He postulated [58] the following general mechanism for the reaction.



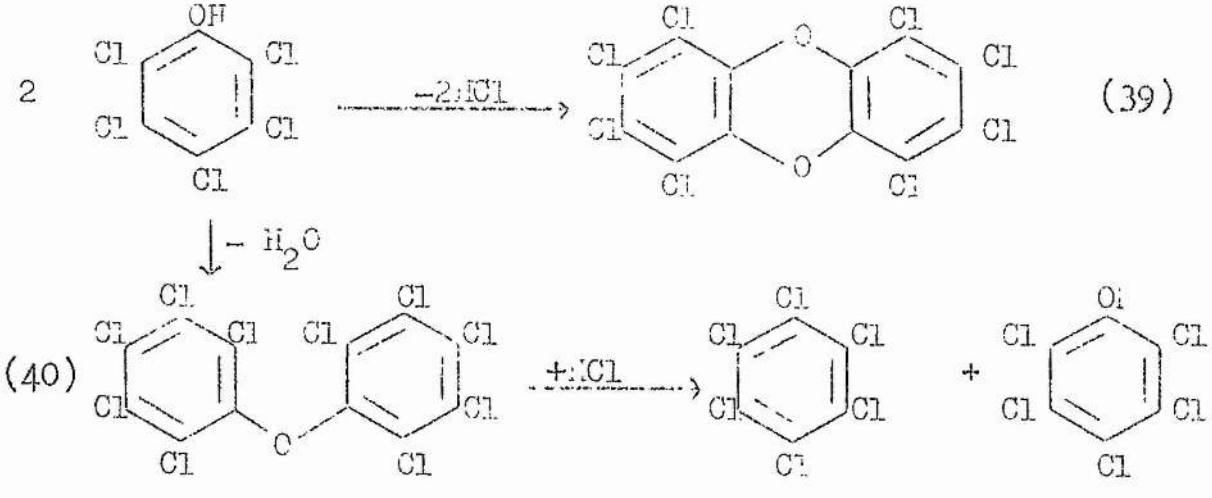
The role of iodine in the polymerization of the sodium and potassium salts could then be explained as an oxidising agent for oxidation of the phenoxy anion to a phenoxy radical.

Dewar and James [59] suggest an alternative mechanism for this reaction which does not involve diradicals, and is, perhaps, more acceptable. In this mechanism a phenoxy radical displaces the halogen atom from a second molecule of the phenol salt. The halogen atom so liberated continues the chain by oxidation of another phenoxy anion.



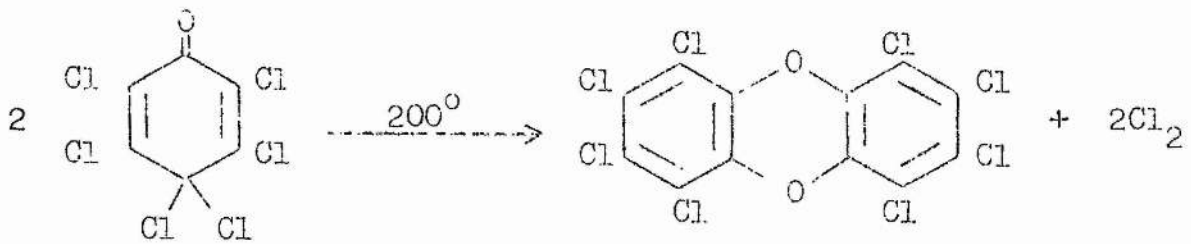
Recently polyphenylene oxide polymers have been obtained by heating potassium o-chlorophenate at 270-280° in the presence of a copper catalyst.[60]

The thermal decomposition of pentachlorophenol and its alkali metal salts has been studied in rather more detail than that of most o-halophenols. As stated above, the reaction was first reported by Merz and Weith[52] although they did not assign a structure to the product which they obtained. About twelve years ago Sandermann, Stockmann and Casten[61] reported the reaction with pentachlorophenol and with its sodium salt. They decomposed pentachlorophenol at 300° and obtained hexachlorobenzene and a compound which they identified as octachlorodiphenylene dioxide (39). Using the same conditions they also obtained octachlorodiphenylene dioxide from sodium pentachlorophenate. They suggested that hexachlorobenzene resulted from the decomposition of decachlorodiphenylene oxide (40) formed during the reaction.



Doubt was cast on this explanation by Denivelle and his co-workers,[62] who found that decachlorodiphenylene oxide was not cleaved with hydrogen chloride under the conditions of the decomposition.

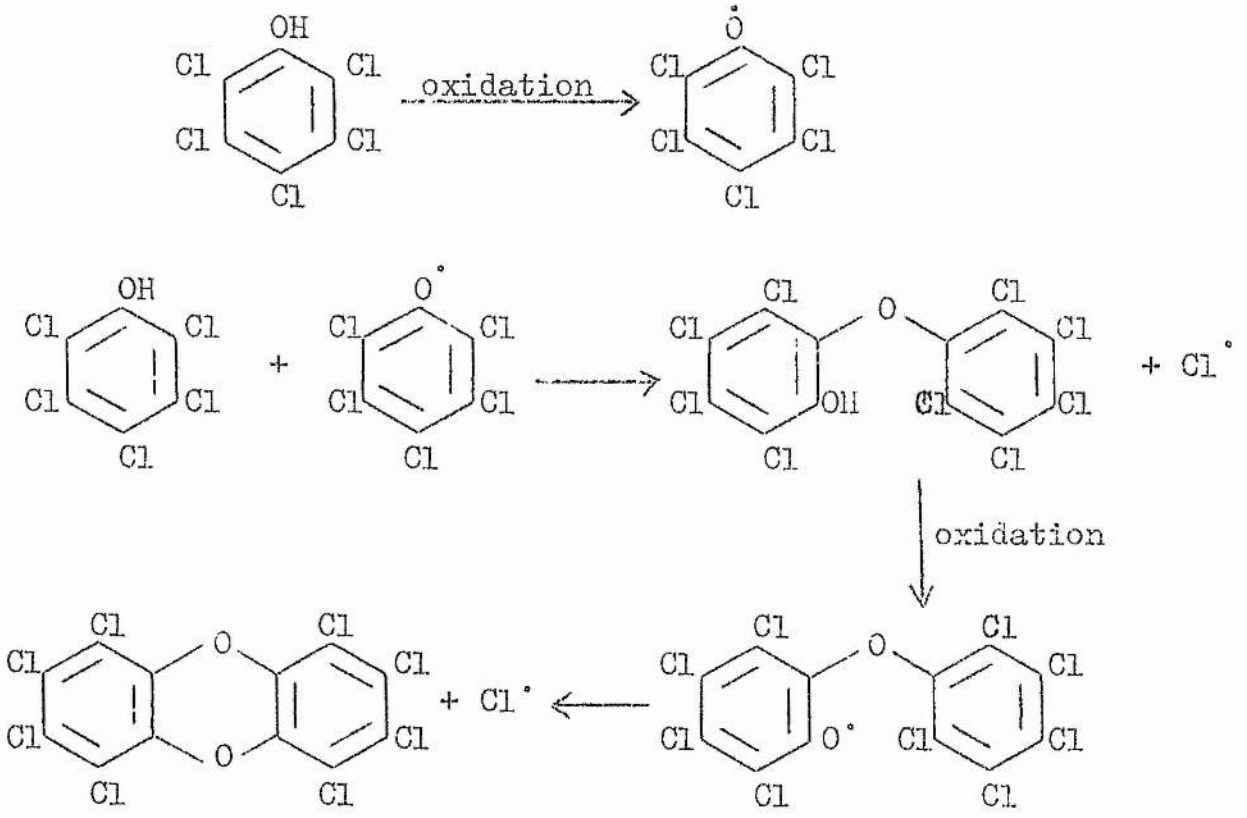
Sandermann and his colleagues obtained octachlorodiphenylene dioxide in very poor yields only. A few years later Kulka[63] succeeded in obtaining almost quantitative yields of the diphenylene dioxide by heating pentachlorophenol with 2,3,4,4,5,6-hexachloro -2,5-cyclohexadienone (41). This had previously[64] been shown to liberate chlorine and give octachlorodiphenylene dioxide, on heating above 200°.



(41)

He suggested that the liberated chlorine oxidised pentachlorophenol to the phenoxy radical which then formed octachlorodiphenylene dioxide, liberating more chlorine in the process to continue the reaction. In support of this he found that chlorine itself, and to a lesser extent bromine and iodine, also increased the yield of diphenylene dioxide.

This is in agreement with mechanisms of Hunter and Dewar for the reactions of trihalophenols and their salts. The full mechanism can be written as follows:



The almost exclusive formation of dimers rather than higher polymers can be explained as a steric effect.

Although this mechanism probably explains the formation of the diphenylene dioxides and polyphenylene oxides satisfactorily in the presence of initiators it does not explain how initiation occurs in their absence, and it is possible that a different mechanism is involved.

4. The Formation and Reaction of Benzyl Radicals

In the investigation described in this thesis the presence of products reminiscent of those formed by reactions of benzyl radicals is reported. A knowledge of the conditions for formation and reaction of benzyl radicals is therefore necessary for a correct interpretation of the results obtained.

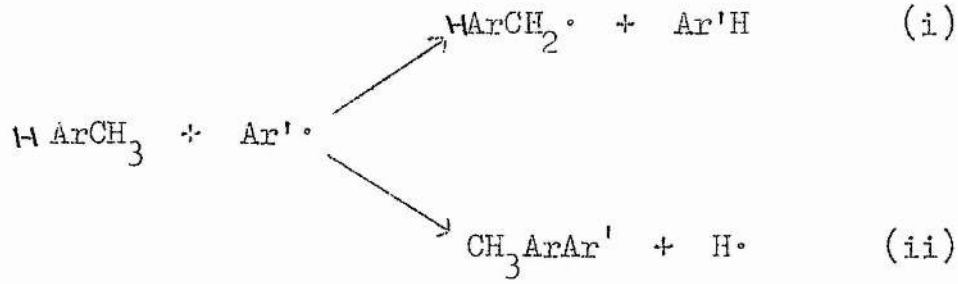
(a) Formation of benzyl radicals from methylbenzenes

Although benzyl radicals can be formed by the pyrolysis of toluene at 700-800°,[65] in less drastic conditions they are usually formed by the abstraction of hydrogen from the methyl side-chain by another radical. Hydrogen abstraction from methylbenzenes by radicals almost always involves abstraction from the methyl group, giving a benzyl radical, rather than abstraction from the aromatic ring to give phenyl radicals.[66] Abstractions of this kind have been reported to occur with a wide variety of radicals, among them phenyl radicals[67] and t-butoxy radicals.[66,68]

$$ArCH_3 + R^{\bullet} \longrightarrow ArCH_2^{\bullet} + RH$$

Although hydrogen abstraction from the aromatic ring does not compete with abstraction from methyl substituents, displacement of hydrogen atoms in the ring by radicals does occur, sometimes as the

major reaction route. The competition between these two reaction paths for substituted phenyl radicals has been studied extensively.



For the reaction of toluene with phenyl radicals, obtained from the decomposition of benzoyl peroxide, reaction (ii) is found to predominate, the ratio of (i):(ii) being 13:87.[67b] Increasing the number of methyl groups in the side-chain or the ring favours the formation of benzyl radicals; thus for ethylbenzene the ratio is 55:45 and for isopropylbenzene it is 60·5:39·5. p-Xylene and mesitylene are also more susceptible to side-chain attack than toluene.[67a]

Substituents in the attacking aryl radical also affect the course of the reaction, electron-withdrawing groups such as nitro and chloro favouring the displacement reaction and electron-donating groups, in particular methyl, favouring hydrogen abstraction.[69]

The effect of substituents in the aromatic ring on the rate of hydrogen abstraction from the side-chain of toluene by various radicals has been studied extensively, and Hammett ρ values have been calculated for these reactions. These are summarised below:

Attacking Radical	ρ	Ref.
$C_6H_5\cdot$	0	70
$Cl\cdot$	-0.66	71
$Br\cdot$	-1.46	72
$(CH_3)_3CO\cdot$	-0.76	73
$CCl_3\cdot$	-1.46	74

These values indicate the electrophilic character of the radicals studied, with the exception of the phenyl radical. The rate of hydrogen abstraction by methyl radicals also appears not to be influenced by polar substituents.[75] For toluene the percentage of attack by methyl radicals at the ring rather than the side-chain is about 25%.[76] Nuclear attack does not seem to be very important with radicals in which the unpaired electron is on an atom other than carbon.

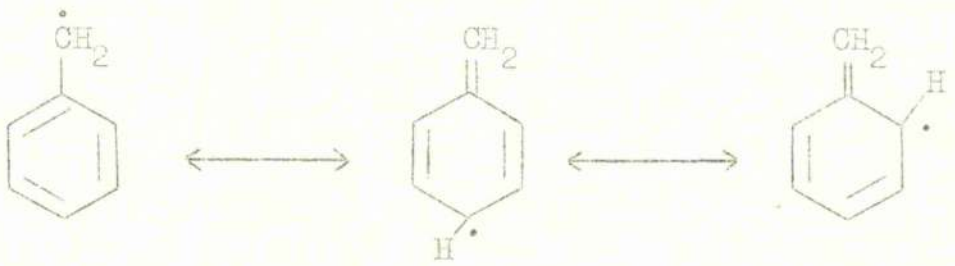
These data suggest that in the systems to be discussed later, involving attack on polymethylbenzenes, frequently by polymethylphenyl radicals, hydrogen abstraction from the side-chain will be the major reaction.

(b) Reactions of benzyl radicals

The reactions undergone by free radicals in solution are to

some extent dependent on the stability of the radicals concerned. Thus very unstable radicals will react rapidly with any molecules available by addition, abstraction, substitution, etc. More stable radicals tend to undergo reactions with other radicals, such as combination or disproportionation, more readily. Benzyl radicals fall into the latter category.

The stability of the benzyl radical can be attributed to resonance as shown:



Evidence for contributions by these resonance structures can be obtained from e.s.r. spectra. The coupling constants due to interactions with protons in the system can be related to the unpaired electron density at the carbon atom to which the proton is attached. The coupling constants for the benzyl radical are as follows:-[77] $a_{H(methylene)}$ 16.4 gauss, $a_{\underline{o}-H}$ 5.1 gauss, $a_{\underline{m}-H}$ 1.6 gauss, $a_{\underline{p}-H}$ 6.3 gauss. These figures indicate some unpaired electron density at the ortho and para positions.

Because of this stability the most common reaction of benzyl radicals is dimerization to give bibenzyls.

$$ArCH_2^{\cdot} + Ar'CH_2^{\cdot} \longrightarrow ArCH_2CH_2Ar'$$

Yields of such products can be used to estimate the extent of formation of benzyl radicals.[66,67,68,69]

Hydrogen abstraction by benzyl radicals is only likely to occur if the resulting radical is of similar or greater stability than the benzyl radical itself, thus hydrogen abstraction from a benzene ring to give a phenyl radical would not be expected. Abstraction of hydrogen from the side-chain of an aromatic compound to give another benzyl radical is thought not to occur by some authors;[78] however Jackson[79] has shown that this reaction does occur in the decomposition of dibenzyl mercury in p-chlorotoluene:

$$Hg(CH_2Ph)_2 \longrightarrow Hg + 2PhCH_2^{\cdot} \quad (i)$$

$$2PhCH_2^{\cdot} \longrightarrow PhCH_2CH_2Ph \quad (ii)$$

$$PhCH_2^{\cdot} + CH_3C_6H_4Cl \longrightarrow PhCH_3 + {\cdot}CH_2C_6H_4Cl \quad (iii)$$

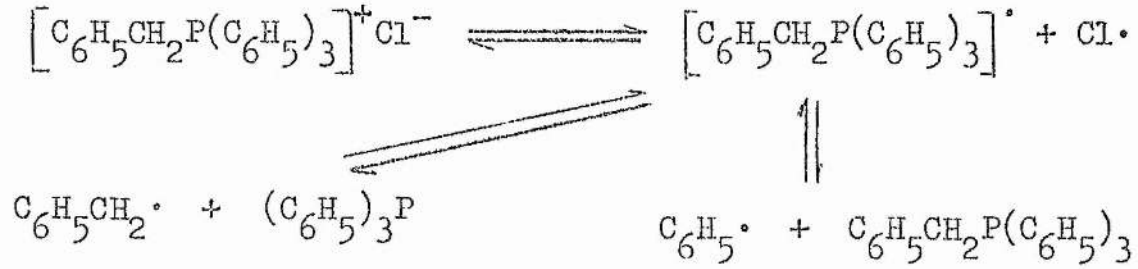
$$PhCH_2^{\cdot} + {\cdot}CH_2C_6H_4Cl \longrightarrow PhCH_2CH_2C_6H_4Cl \quad (iv)$$

$$2{\cdot}CH_2C_6H_4Cl \longrightarrow ClC_6H_4CH_2CH_2C_6H_4Cl \quad (v)$$

Appreciable amounts of the chlorinated bibenzyls were obtained, and an activation energy of 20.3 kcal/mole was calculated for the reaction, suggesting that this reaction would only be of importance at high temperatures.

Homolytic benzylation of aromatic compounds does not usually

occur,[80] although it is postulated in the photolysis of benzyltriphenylphosphonium chloride in a mixture of benzene and ethanol, in which diphenylmethane is formed.[81]

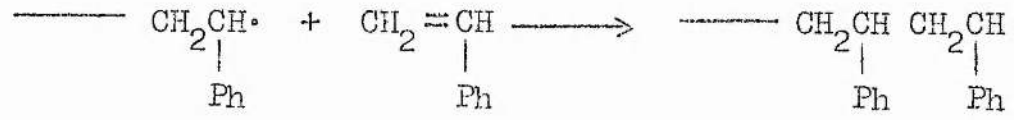


$$PhCH_2\cdot + PhH \longrightarrow PhCH_2Ph$$

$$PhCH_2\cdot + Ph\cdot \longrightarrow PhCH_2Ph$$

Williams considers[80] that phenyl radicals are generally too reactive to undergo dimerisation so that formation of diphenyl methane by combination of phenyl and benzyl radicals is unlikely to occur.

Addition to an olefinic bond is another course of reaction open to benzyl or benzylic radicals. An obvious example of this is in the formation of polystyrene where the chain process involves addition of a benzylic radical to the olefinic bond of styrene:



Walling[82] calculates that the addition of a benzyl radical

to ethylene is exothermic by 1·5 kcal/mole at 25° from consideration of the dissociation energies of the bonds involved.

In the systems to be discussed the temperatures involved are in general very much higher than those used in the investigations mentioned here. For this reason radical transfer and substitution may well be of importance, in addition to the better documented dimerisation and addition reactions.

5. Programme of Research

Bromodurene and bromomesitylene have been shown[15] to be unreactive towards the system sodamide in liquid ammonia, under conditions which would give benzyne intermediates with other aryl halides. An investigation into the reaction of aryl halides with potassium t-butoxide has shown that this reaction also involves aryne intermediates.[23] It has now been shown that bromodurene does react with potassium t-butoxide at elevated temperatures.[83] Accordingly similar systems involving 2,6-dimethylaryl halides and potassium t-butoxide or sodamide have been studied, in order to establish whether the reaction is general in this type of system, and in an attempt to determine the mechanism of the reaction.

It seemed possible that intermediates similar to those

proposed for this reaction might be present in related systems, and the thermal decomposition of the sodium salts of o-halophenols has been studied with this in mind.

EXPERIMENTAL

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Experimental

Gas-Liquid Chromatography: Four instruments were used for g.l.c. analyses: a Perkin-Elmer F.11 chromatograph, with a flame-ionisation detector, using 2m x 2.2mm i.d. packed columns; a Varian Aerograph 1520B chromatograph, with a flame-ionisation detector, using 2m x 2.2mm i.d. packed columns; a Pye Series 104, Model 54, chromatograph with flame-ionisation detector, using 1.5m x 4mm i.d. packed columns; and a Griffin and George D.6 gas-density balance chromatograph, using 2m x 5mm i.d. packed columns. Quantitative measurements were made using either the D.6 instrument with the internal standard technique described by Cadogan and Sadler,[84] or the Pye 104 chromatograph or occasionally the Varian Aerograph 1520B instrument. The response of the flame-ionisation detectors was determined by analysis of standard mixtures.

A Pye Series 105, Model 15, chromatograph was normally used for preparative g.l.c., or occasionally an Aerograph A.700.

Nitrogen was used as carrier gas in all cases, flow rates being those recommended by the manufacturers.

The following stationary phases, supported on 100-120 mesh celite, were used: Carbowax 20M (CAR), neopentylglycol succinate (NPGS), polyethyleneglycol adipate (PEGA), 1,4-butanediol succinate polyester (BDS), silicone oil (SIL) and apiezon L grease (APL).

Proton Magnetic Resonance Spectroscopy: A Perkin-Elmer Model R-10 Nuclear Magnetic Resonance Spectrometer, operating at a frequency of 60 Mc./sec. and a probe temperature of 35.5°, was used. Spectra were determined on solutions of concentration 10-15% w/v. Chemical shifts are recorded as tau (τ) values in parts per million, using tetramethylsilane (τ 10.0) as internal reference.

Infra-red Spectroscopy: Spectra were recorded on Perkin-Elmer Model 237 or 257 Spectrophotometers using thin films of liquid samples, and Nujol mulls of solids. Matched cells (path length indicated) with silver chloride or sodium chloride windows, were used to determine solution spectra.

Mass Spectroscopy: Mass spectra were recorded on an A.E.I. MS 902 mass spectrometer.

Melting Points: The melting points of all new compounds were recorded on a Kofler hot-stage apparatus.

Elemental Analyses: Microanalyses were performed by Mr. J. Bews, University of St. Andrews, and by Weiler and Strauss, Oxford.

Solvents: Common solvents were distilled and dried over sodium wire. Petroleum refers to the fraction b.p. 40-60°. Dry methanol was prepared by the method of Vogel.[85] Cyclohexene was

passed down an alumina column, distilled and stored over sodium wire. Immediately before use it was distilled from sodium in an atmosphere of dry nitrogen.

Reagents: Liquid aryl halides were dried over phosphorus pentoxide, distilled, and stored over molecular sieve (B.D.H. Type 4A), solids were dried in a vacuum desiccator over phosphorus pentoxide. The purity of all aryl halides was checked by g.l.c. Potassium t-butoxide was sublimed, block temperature 210°/0.1 mm. Sodamide (May and Baker) and sodium pentachlorophenate (B.D.H.) were used without purification. Sodium o-bromophenate was prepared from sodium methoxide and o-bromophenol, and the residue after removal of solvent and excess phenol was used without further purification. Other reagents were purified by distillation or crystallisation.

1. Preparation of Halomethylbenzenes

(a) Bromomesitylene. Bromomesitylene was prepared from mesitylene by the method of Smith[86] in 73% yield, and had b.p. 103-105°/10 mm.

(b) Bromodurene. Durene was brominated by the method of Smith and Moyle,[87] and recrystallised from ethanol m.p.60-60.5°

(lit.,[87] 60.5°), in 66% yield.

(c) Bromoisodurene. isoDurene was prepared from 2,4,6-trimethylphenyl magnesium bromide and dimethyl sulphate as described by Smith[88] in 41% yield, b.p. 80-84°/13 mm. It was brominated in 65% yield by the method of Smith and Moyle[87] and had b.p. 120-125°/10 mm.

(d) Bromopentamethylbenzene. Pentamethylbenzene was prepared from mesitylene by the method of Crawford and Magill[89] in 20% yield. On recrystallisation from ethanol it had m.p. 45-47° (lit.,[89] 52-53°). It was brominated by the method of Smith and Nichols[90] in 65% yield. After recrystallisation from chloroform and ethanol it had m.p. 157-158° (lit.,[90] 159-160°).

(e) Chlorodurene. This was prepared by a modification of the method of Smith and Moyle.[91] Durene (120 g., 0.895 mole) was dissolved in chloroform (500 ml.) and the solution was cooled to 0°. A slow stream of chlorine was passed through the solution until 40 g., 0.57 mole, had been taken up. Chloroform was removed under vacuum and the product was steam distilled. Crude chlorodurene was extracted from the distillate with chloroform, the extract was dried over magnesium sulphate and distilled to give chlorodurene (42 g., 30%) b.p. 115-120°/15 mm. On recrystallisation from ethanol this had m.p. 44-45° (lit.,[91] 47.5-48°).

(f) Iododurene. A solution of durene (35 g., 0.26 mole) and iodine (21 g., 0.165 mole) in glacial acetic acid (300 ml.) was stirred at room temperature, and fuming nitric acid (18 ml., 0.41 mole, sp.gr. 1.5) was added slowly, over thirty minutes. Stirring was continued for a further 10 minutes when iododurene precipitated from the solution and the brown colour of the iodine was discharged. The product was filtered and washed with water. The solid was dissolved in ether, dried over magnesium sulphate and distilled to give iododurene (42 g., 67%), b.p. 144-146°/10 mm. On recrystallisation from ethanol this had m.p. 79-80° (lit.,[92] 78.5-79.5°).

1-Bromo-2,6-dimethylbenzene obtained from Koch-Light had b.p. 95-97°/22 mm.

2. Preparation of Bibenzyls (n.m.r. data for these compounds are summarised in Table I, page 57)

(a) Preparation of 3,5,3',5'-tetramethylbibenzyl.

Di-t-butyl peroxide (3.5 g., 0.024 mole) and mesitylene (45 g., 0.375 mole) were stirred at 120° for 14 hours in an atmosphere of dry nitrogen. The temperature was raised to 155°, and stirring continued for 8 hours. Excess mesitylene was removed under reduced pressure and the residue was distilled to give 3,5,3',5'-tetramethyl-bibenzyl (2.38 g., 0.01 mole, 41.6%). On crystallisation from ethanol this had m.p. 74.5° (lit.,[93], 72-73°). (Found: C, 90.5;

H, 9.5. Calc. for $C_{18}H_{22}$: C, 90.75; H, 9.25%.)

(b) Preparation of dibromo-3,5,3',5'-tetramethylbibenzyl isomers. This was prepared in the same way from di-t-butyl peroxide (3 g., 20.5 mmoles) and bromomesitylene (20 g., 100.5 mmoles). After removal of excess bromomesitylene under vacuum the residue was chromatographed on an alumina column. Elution with petroleum gave a mixture of isomeric dibromo-3,5,3',5'-tetramethylbibenzyls (3.04 g., 7.7 mmoles, 37.4%), which was recrystallised from ethanol. (Found: C, 54.8; H, 5.35. $C_{18}H_{20}Br_2$ requires C, 54.6; H, 5.05%.)

(c) Preparation of bromo-3,5,3',5'-tetramethylbibenzyl isomers. This was prepared in a similar way using di-t-butylperoxide (3.5 g., 0.024 mole), mesitylene (14.5 g., 0.121 mole) and bromomesitylene (24 g., 0.120 mole). Bromomesitylene and mesitylene were removed under vacuum and the residue was chromatographed on alumina. Elution with petroleum gave a white solid (0.77 g.), which was shown by g.l.c. examination (2% NPGS, 225°) to contain a mixture of tetramethylbibenzyl, bromotetramethylbibenzyl and dibromotetramethylbibenzyl. Preparative g.l.c. (8 ft. x 0.375 in. i.d. aluminium column containing 2% NPGS on celite at 225°) yielded a sample of isomeric bromo-3,5,3',5'-tetramethylbibenzyls. (Found: C, 68.2; H, 6.8. $C_{18}H_{21}Br$ requires C, 68.2; H, 7.0%.)

(d) Preparation of 4,4'-dimethylbibenzyl. This was prepared

in 13% yield by the method described for the preparation of 3,5,3',5'-tetramethylbibenzyl. On recrystallisation from ethanol it had m.p. 83-83.5° (lit.,[94] 80-81°).

(e) Preparation of 3,3'-dimethylbibenzyl. This was prepared in a similar manner from di-t-butyl peroxide (4 g., 0.0274 mole) and m-xylene (25.5 g., 0.240 mole). Distillation gave 3,3'-dimethylbibenzyl (2.18 g., 0.0138 mole, 38%) b.p. 95-97°/0.05 mm. (Found: C, 91.6; H, 8.9. $C_{16}H_{18}$ requires C, 91.4; H, 8.6%.)

(f) Preparation of 2,2'-dibromo-3,3'-dimethylbibenzyl. This was prepared in 39% yield by the same method. On recrystallisation from ethanol it had m.p. 116-117°. (Found: C, 52.0; H, 4.55. $C_{16}H_{16}Br_2$ requires C, 52.2; H, 4.4%.)

(g) Preparation of dichloro-2,4,5,2',4',5'-hexamethylbibenzyl isomers. This was prepared similarly from di-t-butyl peroxide (3 g., 0.0205 mole) and chlorodurene (35 g., 0.206 mole). After removal of chlorodurene under vacuum, the residue was chromatographed on alumina. Elution with petroleum gave a mixture of isomeric dichloro-2,4,5,2',4',5'-hexamethylbibenzyls (2.90 g., 0.0087 mole, 42%) which was recrystallised from chloroform and ethanol as white needles. (Found: C, 71.4; H, 7.4. $C_{20}H_{24}Cl_2$ requires C, 71.7; H, 7.2%.)

(h) Preparation of chloro-2,4,5,2',4',5'-hexamethylbibenzyl

isomers. This was prepared similarly from di-t-butyl peroxide (3.2 g., 0.0219 mole), chlorodurene (17.3 g., 0.103 mole) and durene (13.8 g., 0.103 mole). Distillation gave a mixture (1.26 g.) of dichloro-2,4,5,2',4',5'-hexamethylbibenzyl, chloro-2,4,5,2',4',5'-hexamethylbibenzyl, and 2,4,5,2',4',5'-hexamethylbibenzyl. Preparative g.l.c. (7 ft. x 0.375 in. o.d. column packed with 5% APL on celite at 225°) gave a pure sample of chloro-2,4,5,2',4',5'-hexamethylbibenzyl isomers, which was sublimed, block temp. 150°/0.1 mm. (Found: C, 80.1; H, 8.7. $C_{20}H_{25}Cl$ requires C, 79.9; H, 8.4%.)

(i) Preparation of diiodo-2,4,5,2',4',5'-hexamethylbibenzyl isomers. This was prepared in a similar manner from di-t-butyl peroxide (2 g., 0.0137 mole) and iododurene (32.7 g., 0.136 mole). Iododurene was removed under vacuum and the residue was chromatographed on alumina. Elution with petroleum gave three fractions, all white solids, as follows:- (i) 1.056 g.; (ii) 0.673 g.; (iii) 0.971 g. Examination by g.l.c. (2% NPGS, 225°) showed (i) and (iii) to be almost pure samples of compounds with different g.l.c. retention times, while (ii) was a mixture of the two. Fractions (i) and (iii) were recrystallised separately from light petroleum (b.p. 60-80°) and had m.p. (i) 120-121°, (iii) 156-157°. N.m.r. and mass spectra indicated that these were isomeric diiodo-2,4,5,2',4',5'-hexamethylbibenzyls. (Found: (i) C, 47.2;

H, 5.0. (iii) C, 46.6; H, 5.0. $C_{20}H_{24}I_2$ requires C, 46.5; H, 4.7%.)

(j) Preparation of iodo-2,4,5,2',4',5'-hexamethylbibenzyl isomers. This was prepared similarly from di-t-butyl peroxide (4 g., 0.0274 mole), durene (13.8 g., 0.103 mole) and iododurene (25 g., 0.104 mole). Iododurene and durene were removed under vacuum, and the residue (11.3 g.) containing a mixture of 2,4,5,2',4',5'-hexamethylbibenzyl, iodo-2,4,5,2',4',5'-hexamethylbibenzyl and diiodo-2,4,5,2',4',5'-hexamethylbibenzyl, was purified by preparative t.l.c. on 1 mm. thick silica plates. The plates were developed in a mixture of benzene and petroleum (1:10) and product bands were detected in ultra-violet light after the plates had been sprayed with fluorescein solution. A sample of iodo-2,4,5,2',4',5'-hexamethylbibenzyl was obtained, which was shown, on examination by g.l.c. (2% NPGS, 225°) to be contaminated with hexamethylbibenzyl. Attempted purification was unsuccessful. Mass spectrum: see Appendix.

(k) Preparation of isomeric octamethylbibenzyls. This was prepared from di-t-butyl peroxide (3 g., 0.0205 mole) and pentamethylbenzene (30 g., 0.2025 mole). Distillation gave octamethylbibenzyl (2.95 g., 0.01 mole, 49%) b.p. 144-150°/0.1 mm., which was recrystallised from petroleum. (Found: C, 89.6; H, 10.7. $C_{22}H_{30}$ requires C, 89.8; H, 10.4%.)

(l) Preparation of dibromooctamethylbibenzyl isomers. These were prepared from di-t-butyl peroxide (3.4 g., 0.0233 mole) and bromopentamethylbenzene (18 g., 0.0795 mole) as in the previous experiments. The product was chromatographed on alumina and elution with petroleum gave bromopentamethylbenzene (14.3 g.), followed by a mixture of isomeric dibromooctamethylbibenzyls (1.178 g., 0.00261 mole, 11.2%). This was recrystallised from chloroform and ethanol. (Found: C, 58.4; H, 6.3. $C_{22}H_{28}Br_2$ requires C, 58.6; H, 6.4%.)

(m) Preparation of bromooctamethylbibenzyl isomers. These were prepared similarly from di-t-butyl peroxide (2 g., 0.0137 mole), bromopentamethylbenzene (8 g., 0.0352 mole) and pentamethylbenzene (5.2 g., 0.0351 mole). Bromopentamethylbenzene and pentamethylbenzene were removed under vacuum, and the residue, containing a mixture of octamethylbibenzyls, bromooctamethylbibenzyls and dibromooctamethylbibenzyls, was separated by preparative t.l.c. on 1 mm. thick silica plates. A mixture of petroleum and benzene (20:1) was used as developing solvent and products were detected by the fluorescence produced in ultra-violet light when the plates were sprayed with fluorescein. A sample of isomeric bromooctamethylbibenzyls was obtained which was sublimed, block temp. 160-170°/0.1 mm. This was contaminated with octamethylbibenzyl and dibromooctamethylbibenzyl.

Mass spectrum: see Appendix.

(n) Preparation of hexamethylbibenzyl isomers from isodurene. These were prepared similarly from di-t-butyl peroxide (3 g., 0.0205 mole) and isodurene (26 g., 0.194 mole). Distillation gave a mixture of isomeric hexamethylbibenzyls (1.80 g., 0.0068 mole, 33%), b.p. 116-124°/0.1 mm. This was a colourless viscous oil which solidified on standing. (Found: C, 90.1; H, 10.1. $C_{20}H_{26}$ requires C, 90.2; H, 9.8%.)

(o) Preparation of brominated hexamethylbibenzyl isomers based on isodurene. These were prepared similarly from di-t-butyl peroxide (1 g., 0.00685 mole), isodurene (5.g., 0.0373 mole) and bromoisodurene (8 g., 0.0376 mole). isoDurene and bromosiodurene were removed under vacuum. Preparative g.l.c. (7 ft. x 0.0375 in. o.d. column packed with 5% APL on celite at 225°) on the residue gave samples of bromohexamethylbibenzyl, a colourless oil b.p. 150°/0.1 mm.(block temperature)(Found: C, 69.5; H, 7.5. $C_{20}H_{25}Br$ requires C, 69.55; H, 7.25%), and dibromohexamethylbibenzyl, a white solid, which was distilled, b.p. 165°/0.1 mm. (block temperature).

Mass spectrum: see Appendix.

TABLE I: /.....

TABLE I: ^{1}H N.m.r. Spectral Data for Halomethylbibenzyls

(τ values)

Substituents	Aromatic[a]	$-CH_2-CH_2-$[b]	Methyl[c]
1) 3,5,3',5'Me	3.31	7.26	7.75
2) Br; 3,5,3',5'Me	3.04–3.30	6.95–7.25	7.50–7.79
3) diBr; 3,5,3',5'Me	3.10–3.35	7.06,7.30	7.56–7.82
4) 4,4'Me	3.04	7.19	7.71
5) 3.3'Me	2.92–3.25	7.22	7.75
6) 2,2'Br; 3,3'Me	3.03	6.99	7.58
7) Cl; 2,4,5,2',4',5'Me	3.21	7.15–7.34	7.65–7.85
8) diCl; 2,4,5,2',4',5'Me	3.05–3.20	7.05	7.55–7.80
9) I; 2,4,5,2',4',5'Me	3.08	7.22	7.44–7.85
10) diI; 2,4,5,2',4',5'Me (i)	3.19	6.79	7.51,7.68,7.81
(ii)	2.92,3.08	6.90–7.15	7.25–7.66
11) hexa Me	3.28	7.30	7.65–7.94
12) Br; hexa Me	3.16–3.38	7.05–7.45	7.59–7.95
13) diBr; hexa Me	3.20	6.98–7.39	7.51–7.96
14) octa Me	3.02–3.21	7.20	7.50–7.85
15) Br; octa Me	3.05–3.20	6.95–7.25	7.41–7.82
16) diBr; octa Me	—	6.93–7.23	7.38–7.95

Solvent: CCl_4 (1–7,11–13) $CDCl_3$ (8–10,14–16).

(a) singlet (1,4); broad singlet (7,9,10 i,11,13); two singlets (10 ii); otherwise complex.

(b) 4H, singlet (1,4,5,6,10 i); broad singlet (8,9,11,12,14); two singlets (3); otherwise complex.

(c) singlet (1,4,5,6); otherwise complex.

3. Miscellaneous Reactions

(a) Preparation of octachlorodiphenylene dioxide. This was prepared by the method of Kulka[63] in 33% yield, using bromine, two drops added every hour for six hours, as initiator. On recrystallisation from 1,2,4-trichlorobenzene it had m.p. 333-335° (lit.,[63] 330-332°).

I.r. (Nujol): 1555, 1307, 1009, 992, 861, 851, 727, 670 $cm.^{-1}$

(hexachlorobutadiene): 1440, 1400 $cm.^{-1}$

This is identical to the spectrum reported by Denivelle, Fort and Van Hai.[62]

(b) Preparation of 2,3,4,5-tetrachlorophenol. 2,3,4,5-Tetrachloroanthranilic acid was prepared in 30% yield from tetrachlorophthalic anhydride by the method of Villiger and Blangey.[95] On recrystallisation from petroleum it had m.p. 178-179° (lit.,[95] 180-183°).

I.r. (Nujol): 3480, 3360, 1670, 1595, 1290 $cm.^{-1}$

This was diazotised and decomposed by the method described by Howe,[96] to give 2,3,4,5-tetrachlorophenol in 28% yield, which on recrystallisation from light petroleum (b.p. 60-80°) had m.p. 115-116° (lit.,[96] 116-117°).

N.m.r. ($CDCl_3$): τ 2.90 (singlet, 1H, aromatic H), 4.35 (singlet, 1H, OH).

I.r. (Nujol): 3520,1590,1560,1280,1200,1160,1100,990,865,855,740 $cm.^{-1}$

(c) Preparation of 2,3,5,6-tetrachlorophenol. 2,3,5,6-Tetrachloronitrobenzene (10 g., 39 mmoles) in glacial acetic acid (60 ml.) was added to a solution of stannous chloride (40 g., 177 mmoles) in concentrated hydrochloric acid (50 ml.). The mixture was heated to the reflux temperature for two hours and allowed to cool, when white needles of 2,3,5,6-tetrachloroaniline were precipitated. These were filtered, washed with water, dried and recrystallised from petroleum (5.2 g., 22.5 mmoles, 57%) m.p. 98-99° (lit.,[97] 107-108°).

Ir. (Nujol): 3500, 3400, 1605, 1290, 1255, 1110, 1100, 970, 820, 680 $cm.^{-1}$

This was diazotised and decomposed by the method of Tiessens[98] in 16.5% yield to give 2,3,5,6-tetrachlorophenol, which on recrystallisation from petroleum had m.p. 112-113° (lit.,[98] 115°).

N.m.r. ($CDCl_3$): τ 2.83 (singlet, 1H, aromatic), 3.82 (broad singlet, 1H, OH).

I.r. (Nujol): 3480, 1550, 1290, 1210, 1165, 1110, 960, 856, 650 $cm.^{-1}$

(d) Preparation of bromotrimethylbenzyl bromide. Bromodurene (30 g., 0.141 mole) and N-bromosuccinimide (20 g., 0.112 mole) in carbon tetrachloride (100 ml.) was heated to the reflux temperature, and one or two crystals of benzoyl peroxide were added. The system was maintained at the reflux temperature for three hours. The succinimide precipitated during the reaction was filtered off, and

carbon tetrachloride was removed from the filtrate under vacuum. Distillation gave a mixture of 2-bromo-3,4,6-trimethylbenzyl bromide, and 3-bromo-2,4,5-trimethylbenzyl bromide (22.0 g., 0.075 mole, 67.0%) b.p. 92-96°/0.1 mm. (Found: C, 41.1; H, 4.2. $C_{10}H_{12}Br_2$ requires C, 41.1; H, 4.1%.)

N.m.r. (CCl_4): τ 3.05, 3.28 (2 singlets, 1H, aromatic), 5.39, 5.64 (2 singlets, 2H, methylene), 7.39-7.81 (complex, 9H, methyl).

(e) Preparation of isobutyl toluene-p-sulphonate. This was prepared in 35% yield by the method of Roos, Gilman and Beaber,[99] b.p. 105-106°/0.15 mm.

N.m.r. (CCl_4): τ 2.50 (centre of A_2B_2 system, 4H, aromatic) 6.28 (doublet, J = 6 c/s, 2H, $-CH_2-$), 7.57 (singlet, 3H, aromatic methyl), 7.75-8.42 (multiplet, 1H, $-CH<$), 9.13 (doublet, J = 7 c/s, 6H, aliphatic methyl).

(f) Preparation of 2-bromo-3-methylisopentylbenzene. 2-Bromo-3-methylbenzyl bromide was prepared in 77% yield by the method described in (d). 2-Bromo-3-methylbenzyl magnesium bromide was prepared by the slow addition of bromomethylbenzyl bromide (6.8 g., 25.8 mmoles) in dry ether (5 ml.) to a stirred suspension of magnesium (0.60 g., 24.7 mmoles) in dry ether (7 ml.) in an atmosphere of dry nitrogen. When most of the magnesium had dissolved a solution of isobutyl toluene-p-sulphonate (11 g., 48.2 mmoles) in dry ether (10 ml.) was

added slowly with stirring and the solution was warmed. Stirring was continued for four hours, and then dilute hydrochloric acid (2M) was added gradually until a clear solution was obtained. The layers were separated and the aqueous layer was extracted with ether. The organic layer and the ether extract were combined, dried over magnesium sulphate and ether was removed under vacuum. The residue was distilled to give a colourless liquid (0.98 g.) b.p. 142-148°/15 mm., which was chromatographed on alumina. Elution with petroleum gave 2-bromo-3-methylisopentylbenzene (0.71 g., 2.95 mmoles, 11.4%) which was redistilled b.p. 130-133° (block temperature)/12 mm. (Found: C, 59.7; H, 7.3. $C_{12}H_{17}Br$ requires C, 59.8; H, 7.1%.)

N.m.r. (CCl_4): τ 3.05 (singlet, 3H, aromatic), 7.08-7.45 (half of A_2X_2 system, 2H, Ar-CH_2-), 7.62 (singlet, 3H, aromatic methyl), 7.98-8.75 (half of A_2X_2 system with complex absorption superimposed, 3H, $-CH_2-\dot{C}H$), 9.03 (doublet, J = 5 c/s, 6H, aliphatic methyl).

Mass spectrum: see Appendix.

(g) Preparation of a mixture of 2-chloro-3,4,6-trimethylisopentylbenzene and 3-chloro-2,4,5-trimethylisopentylbenzene. Chlorotrimethylbenzyl bromide was prepared by the method described in (d) in 68% yield, b.p. 84-86°/0.05 mm.

N.m.r. (CCl_4): τ 3.11, 3.24 (2 singlets, 1H, aromatic), 5.47, 5.70 (2 singlets, 2H, methylene), 7.55-7.85 (complex, 9H, methyl).

Chlorotrimethylisopentylbenzene was prepared by the procedure described in the previous experiment, from chlorotrimethylbenzyl bromide (5.4 g., 21.8 mmoles). Elution from an alumina column with petroleum gave a colourless liquid (1.11 g.) which, on examination by g.l.c. (2% NPGS, 130° for 3 mins., programmed at 16°/min. to 225°), was shown to contain chlorotrimethylisopentylbenzene and several impurities. Preparative g.l.c. (15 ft. x 0.375 in. o.d. glass column containing 10% CAR on celite at 180°) gave a sample of a mixture of 2-chloro-3,4,6-trimethylisopentylbenzene and 3-chloro-2,4,5-trimethylisopentylbenzene which was distilled b.p. 150-152° (block temperature)/12 mm. (Found: C, 73.5; H, 9.25. $C_{14}H_{21}Cl$ requires C, 74.95; H, 9.35%.)

N.m.r. (CCl_4): τ 3.31 (singlet, 1H, aromatic), 7.15-7.60 (half of A_2X_2 system, 2H, Ar-CH_2-), 7.65-7.90 (complex, 9H, aromatic methyl), 8.18-8.83 (half of A_2X_2 system with complex absorption superimposed, 3H, $-CH_2-\overset{|}{C}H$), 9.05 (doublet J = 6 c/s, 6H, aliphatic methyl).

Mass spectrum: see Appendix.

(h) Preparation of (tetramethylphenyl)cyclohexylmethane. Pentamethylbenzene (10 g., 67.5 mmoles), cyclohexene (4.6 ml., 3.73 g., 45.5 mmoles) and benzoyl peroxide (5.4 g., 22.3 mmoles)

were stirred, and warmed to 80-100° in an atmosphere of nitrogen. After three hours a further portion of benzoyl peroxide (5.4 g., 22.3 mmoles) was added, stirring was continued, and the temperature was maintained in the range 80-100° overnight. The product was distilled to remove volatile components and the residue (10.8 g.) was chromatographed on alumina. Elution with petroleum gave a colourless oil (0.41 g.). Preparative g.l.c. (7 ft. x 0.375 in. o.d. glass column containing 10% PEGA on celite at 170° for 50 mins., programmed at 24°/min. to 200°) on this oil gave a sample of (tetramethylphenyl)cyclohexenylmethane. (Found: C, 87.0; H, 10.6. $C_{17}H_{24}$ requires C, 89.4; H, 10.6%.)

N.m.r. (CCl_4): τ 3.33 (singlet, 1H, aromatic), 4.39-4.58 (complex, 2H, -CH=CH-), 7.30-7.58 (complex, 2H, benzyl), 7.84 (singlet, 12H, aromatic methyl), 7.95-9.08 (complex, 7H, cyclohexyl).

A portion of this compound was catalytically hydrogenated using a palladium on charcoal catalyst to give (tetramethylphenyl)-cyclohexylmethane which was redistilled b.p. 78°/0.1 mm. (block temperature). (Found: C, 88.4; H, 11.7. $C_{17}H_{26}$ requires C, 88.6, H, 11.4%.)

(i) Preparation of bicyclohex-2,2'-enyl. This was prepared by the method of Farmer and Moore[100] from cyclohexene and di-t-butyl peroxide in 46% yield, b.p. 50-52°/0.4 mm.

N.m.r. (CCl_4): τ 4.46 (broad singlet, 4H, -CH=CH-), 7.60-9.02 (complex, 14H, methylene).

G.l.c. (2% NPGS, 101°) showed this product to be one compound only.

(j) Isomerisation of bicyclohexenyl with potassium t-butoxide. Bicyclohex-2,2'-enyl (1 g., 6.2 mmoles) potassium t-butoxide (0.75 g., 6.7 mmoles) and cyclohexene (20 ml.) were heated at 220° in an autoclave for 100 hours. The reaction mixture was washed with water, dried over magnesium sulphate, and cyclohexene was removed under vacuum. Distillation gave bicyclohexenyl (0.8 g.) b.p. 110-112°/13 mm. Examination by g.l.c. (2% NPGS, 101°) showed that the sample contained products with the same retention times and in similar proportions to a sample of bicyclohexenyl isolated by Dr. Sharp from the reaction of bromodurene and potassium t-butoxide in cyclohexene.

(k) Thermal stability of 3,3'5,5'-tetramethylbibenzyl. 3,3',5,5'-Tetramethylbibenzyl (0.66 g., 2.8 mmoles) in mesitylene (20 ml.) was heated at 250° in an autoclave for 5 days. Mesitylene was removed from the product to leave a residue (0.58 g.) which was recrystallised from ethanol m.p. 72-73°. N.m.r. was indistinguishable from that of 3,3',5,5'-tetramethylbibenzyl and showed no peak at 6.15 τ indicating that 2,3',4,5',6-pentamethyldiphenylmethane was absent.

4. Reactions of Halomethylbenzenes with Strong Base

Unless otherwise stated these reactions were carried out in an autoclave heated to 220° for 100 hours. In general the product mixture was washed from the reaction vessel with a mixture of ether and water, and the aqueous layer was continuously extracted with ether. Measured portions of the ethereal solution were removed for analysis by g.l.c., and unless otherwise indicated yields are recorded as moles per 100 moles of base (m/100 m).

Yield of halide ion was determined gravimetrically as silver halide.

(a) Reaction of bromo-2,6-dimethylbenzene with potassium t-butoxide. Bromo-2,6-dimethylbenzene (35.2 g., 190 mmoles) and potassium t-butoxide (6.42 g., 57.3 mmoles) were allowed to react as previously described. Measured samples of the product mixture were withdrawn, and the bulk of the solution (47.7 mmoles of base) was distilled to give six fractions:- (i) a colourless liquid (2.243 g.) b.p. 20°/112 mm. to 48°/50 mm.; (ii) a colourless liquid (4.993 g.) b.p. 48°/40 mm. to 95°/22 mm.; (iii) a colourless liquid (15.982 g.) b.p. 95-100°/22 mm.; (iv) a colourless liquid (0.800 g.) b.p. 100-120°/15 mm.; (v) a pale-yellow liquid (0.939 g.) b.p. 30-90°/0.05 mm.; (vi) a yellow solid (0.360 g.) b.p. 100-155°/0.05 mm. Examination of these fractions by g.l.c.

(2% NPGS, 35° for 5 mins., programmed at 15°/min. to 215°)

suggested that fraction (i) consisted of m-xylene; this was confirmed by comparison of its i.r. spectrum with that of an authentic sample. Fractions (ii) and (iii) contained mixtures of m-xylene and bromo-2,6-dimethylbenzene. Fractions (iv) and (v) contained another product which was isolated by preparative g.l.c. (15 ft. x 0.375 in. o.d. glass column containing 10% CAR on celite at 175°), and redistilled to give a colourless liquid b.p. 125-135° (block temp.)/12 mm.

N.m.r. (CCl_4): τ 3.04 (s, 3H), 7.05-7.50 (complex, 2H), 7.63 (s, 3H), 8.08-8.66 (complex, 3H), 9.03 (doublet, J = 5.5 c/s, 6H).

Mass spectrum: see Appendix. (Found: C, 60.1; H, 7.2%.)

This was identified as bromo-2-methyl-6-isopentylbenzene, which was confirmed by comparison with an authentic sample. Fraction (vi) contained bromo-2-methyl-6-isopentylbenzene and a complex mixture of high boiling compounds which were not isolated. Measured portions of the reaction mixture were analysed by g.l.c. (2% NPGS, 35° for 3 mins., then programmed at 8°/min. to 125°; 80° for 4 mins., then programmed at 12°/min. to 150°) using bromomesitylene as internal standard. The following products were detected: m-xylene (36.5 m/100m.), bromo-2-methyl-6-isopentylbenzene (11.0). Bromoxylene (42.0 mmoles) was consumed during the reaction. Bromide ion (82 m/100 m.) was displaced.

(b) Reaction of bromomesitylene with potassium t-butoxide. Bromomesitylene (37.3 g., 310.5 mmoles) and potassium t-butoxide (6.833 g., 61.0 mmoles) were allowed to react as previously described. After removal of measured portions of the reaction mixture, the bulk of the solution (56.5 mmoles of base) was distilled to give three fractions as follows:- (i) a colourless liquid (2.91 g.) b.p. 62-72°/15 mm.; (ii) a colourless liquid (19.64 g.) b.p. 104-8°/15 mm.; (iii) a yellow oil (1.72 g.) b.p. 32-162°/0.1 mm. Examination of these fractions by g.l.c. (2% NPGS, 74° for 3 mins. programmed at 12°/min. to 150°; 140° for 3 mins. programmed at 16°/min. to 225°; 10% SIL, 160°) showed that fraction (i) contained a mixture of mesitylene and bromomesitylene, and fraction (ii) was pure bromomesitylene. Fraction (iii) contained a complex mixture of higher boiling products. Preparative g.l.c. (7 ft. x 0.375 in. o.d. glass column containing 5% APL on celite at 190° for 2 hours then heated at 16° per minute to 230°) on fraction (iii) yielded the following samples:- (i) a liquid which was identified as 2-bromo-3,5-dimethylisopentylbenzene and its isomer from its n.m.r. spectrum;

N.m.r. (CCl_4): τ 3.22 (singlet, 2H), 7.10-7.57 (complex, 2H), 7.6-7.8 (complex, 6H), 8.01-8.76 (complex, 3H), 8.81-9.20 (complex, 6H).

(ii) a liquid which was identified as dibromo-2,3',4,5',6-pentamethyldiphenylmethane from its n.m.r. spectrum;

N.m.r. (CCl_4): τ 3.21 (singlet, 4H), 6.1 (singlet, 2H), 7.55-7.94 (complex, 15H).

(iii) bromo-3,5,3',5'-tetramethylbibenzyl which was identified by comparison of its n.m.r. spectrum with that of an authentic sample; (iv) dibromo-3,5,3',5'-tetramethylbibenzyl which was identified by comparison of its n.m.r. spectrum with that of an authentic sample; (v) a liquid. The n.m.r. spectrum indicated that this was an approximately equimolar mixture of 3,5,3',5'-tetramethylbibenzyl and 2,3',4,5',6-pentamethyldiphenylmethane.

N.m.r. (CCl_4): τ 3.09-3.52 (complex, 5.5H), 6.15 (singlet, 1H), 7.26 (singlet, 2H), 7.55-7.92 (complex, 13.5H).

Measured portions of the reaction mixture were analysed by g.l.c. (2% NPGS, 74° for 3 mins., then programmed at 12°/min. to 150°; 145° for 9 mins., then programmed at 16°/min. to 225°) using bromodurene and bromopentamethylbenzene as internal standards. The following products were detected: mesitylene (32.8 m/100 m.), 3,3',5,5'-tetramethylbibenzyl (0.23), 2,3',4,5',6-pentamethyldiphenylmethane (0.51), bromo-3,3',5,5'-tetramethylbibenzyl (1.8), dibromo-3,3',5,5'-tetramethylbibenzyl (1.45). Bromomesitylene (85 mmoles) was consumed in the reaction and bromide ion (89 m/100 m.) was displaced.

(c) Reaction of chlorodurene with potassium t-butoxide.

Chlorodurene (15.94 g., 94.6 mmoles) and potassium t-butoxide (3.44 g.,

30.7 mmoles) were allowed to react as previously described. Measured portions of the reaction mixture were withdrawn for analysis, and the bulk of the solution (25.2 mmoles of base) was distilled to give the following fractions:- (i) a white solid (0.96 g.) b.p. 80-100°/12 mm.; (ii) a white solid (8.14 g.) b.p. 107-114°/12mm.; (iii) a pale yellow solid (2.69 g.) b.p. 117-132°/12 mm.; (iv) a pale yellow solid (0.49 g.) b.p. 48-118°/0.05 mm.; (v) a yellow solid (0.40 g.) b.p. 120-160°/0.05 mm. Examination by g.l.c. (2% NPGS, 140° for 2½ mins., programmed at 24°/min. to 225°; 10% SIL, 160°) suggested that fractions (i) and (ii) contained mixtures of durene and chlorodurene. Preparative g.l.c. (15 ft. x 0.375 in. o.d. glass column containing 10% CAR on celite at 173°) yielded samples of chlorodurene m.p. 41-42°, mixed with authentic chlorodurene m.p. 41-42°, and a mixture of 1-chloro-2-isopentyl-3,5,6-trimethylbenzene and 1-chloro-3-isopentyl-2,5,6-trimethylbenzene; n.m.r. spectrum was indistinguishable from that of an authentic sample.

Preparative g.l.c. (7 ft. x 0.375 in. o.d. glass column containing 5% APL on celite at 225°) on fraction (v) yielded samples of 2,4,5,2',4',5'-hexamethylbibenzyl, chloro-2,4,5,2',4',5'-hexamethylbibenzyl and dichloro-2,4,5,2',4',5'-hexamethylbibenzyl. N.m.r. spectra of these compounds were identical with those of authentic samples. By g.l.c. analysis (2% NPGS, 125° for 9 mins.,

then programmed at 8°/min. to 215°; 5% PEGA, 95° for 3 mins. then programmed at 8°/min. to 141°) using bromodurene and anthracene as internal standards, of measured portions of the reaction mixture, the following products were detected:- durene (25.3 m/100 m.), chlorotrimethylisopentylbenzene (5.6), 2,4,5,2',4',5'-hexamethylbibenzyl (0.172), chloro-2,4,5,2',4',5'-hexamethylbibenzyl (1.49), dichloro-2,4,5,2',4',5'-hexamethyl bibenzyl (0.91), chlorodurene (46 mmoles) was consumed in the reaction. Chloride (60.9 m/100 m.) was displaced.

(d) Reaction of iododurene with potassium t-butoxide. Iododurene (29.38 g., 122 mmoles) and potassium t-butoxide (4.10 g., 36.5 mmoles) were allowed to react as previously described. Measured portions of the reaction mixture were withdrawn for analysis and the bulk of the solution (31.8 mmoles of base) was distilled to give durene (2.071 g.) b.p. 80-90°/10 mm., m.p. 80-81°, mixed with an authentic sample of durene, m.p. 80-81°, and iododurene (12.52 g.) b.p. 144-146°/10 mm. The residue (7.042 g.) was chromatographed on alumina. Elution with petroleum gave iododurene (2.03 g.) and a white solid (2.63 g.). Examination by g.l.c. (2% NPGS, 225°) suggested that this contained a mixture of 2.4,5,2',4',5'-hexamethylbibenzyl, iodo-2,4,5,2',4',5'-hexamethylbibenzyl and diiodo-2,4,5,2',4',5'-hexamethylbibenzyl. Preparative t.l.c. on 1 mm. thick silica plates using petroleum/benzene (10:1) as

developing solvent gave samples of these compounds. Their identities were confirmed by comparison of n.m.r. spectra with those of authentic compounds.

Measured portions of the reaction mixture were analysed by g.l.c. (2% NPGS, 95° for 3 mins., programmed at 8°/mins. to 155°; 130° for 5 mins. programmed at 16°/min. to 225°) using bromomesitylene and 2,2'-dibromo-3,3'-dimethylbibenzyl as internal standards. The following products were detected: durene (35.5 m/100 m.), 2,4,5,2',4',5'-hexamethylbibenzyl (0.96), iodo-2,4,5,2',4',5'-hexamethylbibenzyl (6.82), diiodo-2,4,5,2',4',5'-hexamethylbibenzyl (4.94). Iododurene (62 mmoles) was consumed during the reaction, and iodide ion (82 m/100 m.) was displaced.

(e) Reaction of bromo-2,3,4,6-tetramethylbenzene with potassium t-butoxide. Bromo-2.3.4,6-tetramethylbenzene (19.9 g., 93.5 mmoles) and potassium t-butoxide (3.51 g., 31.3 mmoles) were allowed to react as described. Measured portions of the reaction mixture were withdrawn for analysis and the bulk (23.1 mmoles of base) was distilled to give 1,2,3,5-tetramethylbenzene (1.03 g.) b.p. 100-110°/16 mm. and bromo-2,3,4,6-tetramethylbenzene (7.01 g.) b.p. 136-138°/16 mm. Preparative g.l.c. (7 ft. x 0.375 in. o.d. glass column containing 5% APL on celite at 225°) yielded samples of isomeric mixtures of hexamethylbibenzyls, bromohexamethylbibenzyls and dibromohexamethylbibenzyls. N.m.r. and mass spectra of

these samples were indistinguishable from those of authentic samples.

Measured portions of the reaction mixture were analysed by g.l.c. (2% NPGS, 105° for 3 mins. then programmed at 16°/min. to 155°; 135° for 8 mins. then programmed at 16°/min. to 225°) using bromopentamethylbenzene and 3,5,3',5'-tetramethylbibenzyl as internal standards. The following products were detected: 1,2,3,5-tetramethylbenzene (32.4 m/100 m.), hexamethylbibenzyl (1.65), bromohexamethylbibenzyl (5.73), dibromohexamethylbibenzyl (4.5). Bromo-2,3,4,6-tetramethylbenzene (48.4 mmoles) was consumed during the reaction, and bromide ion (90.5 m/100 m.) was displaced.

(f) Reaction of bromopentamethylbenzene with potassium t-butoxide. Bromopentamethylbenzene (21.61 g., 95.3 mmoles) and potassium t-butoxide (3.40 g., 30.35 mmoles) were allowed to react as described. Measured portions of the reaction mixture were withdrawn for analysis, and the bulk of the solution (25.00 mmoles of base) was distilled to give pentamethylbenzene (0.67 g.) b.p. 109 - 112° / 10 mm.; identity was confirmed by comparison of its i.r. spectrum with that of an authentic sample, and a mixture of pentamethylbenzene and bromopentamethylbenzene (5.64 g.) b.p. 23-120°/0.1 mm. The residue (9.3 g.) was chromatographed on alumina. Elution with petroleum gave bromopentamethylbenzene

(3.95 g.), and with mixtures of benzene and petroleum a white solid (2.69 g.) was obtained. Examination by g.l.c. (2% NPGS, 225°) suggested that this contained a mixture of isomeric octamethylbibenzyls, bromooctamethylbibenzyls and dibromooctamethylbibenzyls. T.l.c. on silica plates developed in benzene/petroleum (1:10) also showed a mixture of three compounds with Rf values identical to those of the authentic bibenzyls. Attempts to obtain samples of the individual bibenzyls were unsuccessful. Elution with more polar solvents yielded tars.

Analysis by g.l.c. (2% NPGS, 95° for 3 mins. programmed at 16°/min. to 160°; 130° for 7 mins., programmed at 16°/min. to 225°) of measured portions of the reaction mixture using durene and 2,4,5,2',4',5'-hexamethylbibenzyl as internal standards, suggested that the following products were present:- pentamethylbenzene (32.7 m/100 m.), octamethylbibenzyl (4.65), bromooctamethylbibenzyl (20.5), dibromooctamethylbibenzyl (11.90). Bromopentamethylbenzene (43.6 mmoles) was consumed during the reaction and bromide ion (90.5 m/100 m.) was displaced.

(g) Reaction of bromomesitylene with potassium t-butoxide in cyclohexene. Bromomesitylene (6.18 g., 31.05 mmoles), potassium t-butoxide (5.88 g., 52.5 mmoles) and cyclohexene (30 ml.) were allowed to react in an autoclave at 220° for 100 hours. The

product was poured into water, the organic layer was separated and the aqueous layer was extracted with benzene. The organic layer and the benzene extracts were combined, dried over magnesium sulphate and benzene and cyclohexene were removed under vacuum. The residue was distilled to give mesitylene (1.76 g.) b.p. 50-56°/10 mm., which had an i.r. spectrum indistinguishable from that of an authentic sample, and two liquid fractions: (i) (1.20 g.) b.p. 60-94°/10 mm.; (ii) (1.10 g.) b.p. 94-108°/10 mm. Examination of these fractions by g.l.c. (10% APL a. 165°, and 2% NPGS, 110°) suggested that they contained mixtures of mesitylene, bromomesitylene and bicyclohexenyl isomers. Yields of products were determined as follows: mesitylene (60.5 m/100 m. of bromomesitylene), bicyclohexenyl (22.5).

(h) Reaction of chlorodurene with potassium t-butoxide in cyclohexene. Chlorodurene (5.15 g., 30.6 mmoles), potassium t-butoxide (5.682 g., 49.9 mmoles) and cyclohexene (20 ml.) were allowed to react as described previously. Measured portions of the reaction mixture were withdrawn and analysed by g.l.c. (2% NPGS, 110° for 8 mins. then programmed at 12°/min. to 175°; 10% SIL, 160° for 4 mins. programmed at 16°/min. to 200°). The following products were detected:- durene (19.75 m/100 m. of chlorodurene), bicyclohexenyl (23.1), (2,4,5-trimethylphenyl)-cyclohexylmethane (4.5), (2,4,5-trimethylphenyl)-cyclohexenyl-

methane (1.2). Chlorodurene (12.2 mmoles) was consumed. Chloride ion (33.2 m/100 m. of chlorodurene) was displaced. (2,4,5-Trimethylphenyl) cyclohexenylmethane was determined as (2,4,5-trimethylphenyl)-cyclohexylmethane after catalytic hydrogenation of a measured portion of the reaction mixture with a 10% palladium on carbon powder catalyst.

(i) Reaction of bromopentamethylbenzene with potassium t-butoxide in cyclohexene. Bromopentamethylbenzene (9.63 g., 42.4 mmoles), potassium t-butoxide (6.24 g., 57 mmoles) and cyclohexene (60 ml.) were allowed to react in an autoclave at 220° for 2 days. The product was poured into water, the organic layer was separated and the aqueous layer was extracted with ether. The organic layer and the ether extract were combined, and dried over magnesium sulphate, and measured portions were withdrawn for analysis. Cyclohexene and ether were removed from the bulk of the solution (40.3 mmole of bromopentamethylbenzene) under vacuum and the residue (13 g.) was chromatographed on silica. Elution with petroleum gave a liquid (7.88 g.) which examination by g.l c. (10% SIL, 160° and 2% NPGS, 145°) suggested contained a mixture of pentamethylbenzene, bicyclohexenyl and bromopentamethylbenzene, and a solid (0.89 g.). Examination by g.l.c. (10% SIL, 180° and 2% NPGS, 145°) suggested this contained bromopentamethylbenzene and a second compound identified as (tetramethylphenyl) cyclohexylmethane.

Elution with petroleum / benzene (20 : 1) gave an oil (0.74 g.).

N.m.r. (CCl_4): τ 3.32 (singlet, 1H), 4.39-4.49 (multiplet, 2H), 7.20-7.60 (complex, 2H), 7.85 (singlet, 12H), 7.95-9.00 (complex, 7H).

Catalytic hydrogenation of this oil gave a white solid m.p. 43-57°.

N.m.r. (CCl_4): τ 3.34 (singlet, 1H), 7.35-7.62 (complex, 2H), 7.84 (singlet, 12H), 8.10-9.30 (complex, 11H).

Mass spectrum: see Appendix.

This was identified as (tetramethylphenyl)cyclohexylmethane, and the oil as (tetramethylphenyl)cyclohexenylmethane by comparison with an authentic sample. Elution with petroleum / benzene (1 : 1) gave a white solid (0.15 g.) which was recrystallised from light petroleum (b.p. 60-80°).

N.m.r. ($CDCl_3$): τ 3.14 (singlet, 2H), 7.20 (complex, 4H), 7.62-7.80 (complex, 24H).

I.r. spectrum was indistinguishable from that of octamethylbibenzyl.

Elution with more polar solvents yielded tars.

Measured portions of the reaction mixture were analysed by g.l.c. (10% APL, 165°; 2% NPGS, isothermal operation at 90° for ten minutes, then programmed to 225° at 16°/min.) using naphthalene as internal standard, and the following compounds were detected:- pentamethylbenzene (54.0 m/100 m. of bromopentamethyl benzene), isomeric bicyclohexenyls (43.8), (tetramethylphenyl)cyclohexylmethane

(9.1), (tetramethylphenyl)cyclohexenylmethane (12.0), octamethylbibenzyl (1.5). Bromide ion (96.0 m/100m.) was displaced. (Tetramethylphenyl)cyclohexenylmethane was estimated as (tetramethylphenyl)cyclohexylmethane, after catalytic hydrogenation of the sample.

(j) 1. Reaction of bromodurene with sodamide in liquid ammonia. Liquid ammonia (250 ml.) was stirred in a flask cooled to -40° in a cold bath and fitted with an air condenser surrounded by solid carbon dioxide, and with a soda-lime guard tube. Small pieces of sodium were added until a permanent blue colour was obtained, which was then discharged by the addition of a few crystals of ferric nitrate. Sodium (1.29 g., 0.056 g.atom) was added gradually, and stirring was continued for approximately one hour, until the blue coloration had completely disappeared. The temperature was allowed to rise to -30°, bromodurene (10.02 g., 0.047 mole) was added, and the mixture was stirred for six hours. Ammonium chloride (4 g., 0.11 mole) was added cautiously, the system was diluted with ether (50 ml.), and the ammonia was allowed to evaporate. Examination of the reaction mixture by g.l.c. (2% NPGS, 120°) showed that no durene was present.

2. Reaction of bromodurene with sodamide in ether. Sodamide was prepared as in the previous experiment from sodium (1.2 g., 0.052 atom) and liquid ammonia (350 ml.). When the blue colour was

discharged, ether (200 ml.) was slowly added to the system, and the ammonia was allowed to evaporate. When the suspension of sodamide in ether attained room temperature, bromodurene (9.81 g., 0.046 mole) was added, and the system was heated at the reflux temperature overnight, after which wet ether was added cautiously to the reaction mixture. Examination of the reaction mixture by g.l.c. (2% NPGS, 180°) showed that durene was absent.

3. Reaction of bromodurene with sodamide in toluene. Sodamide, prepared from sodium (1.24 g., 0.054 g.atom) and liquid ammonia (300 ml.), and bromodurene (9.99 g., 0.047 mole) were allowed to react in boiling toluene (200 ml.) as described in the previous experiment. Examination of the reaction mixture by g.l.c. (2% NPGS, 185°) showed that durene was absent.

4. Reaction of bromodurene with sodamide in t-butyl benzene. Sodamide (0.055 mole) and bromodurene (9.83 g., 0.046 mole) were allowed to react in boiling t-butyl benzene as described in the previous experiment. Examination of the reaction mixture by g.l.c. (2% NPGS, 180°, 225°) showed that durene was present and that compounds with the same retention times as 2,4,5,2',4',5'-hexamethylbibenzyl, bromohexamethylbibenzyl and dibromohexamethylbibenzyl were also present.

5. Reaction of bromodurene with sodamide. Bromodurene (8.46 g., 39.7 mmoles) and sodamide (0.46 g., 11.8 mmoles) were

allowed to react as described (page 65). Measured samples of the reaction mixture were removed for analysis and the bulk (10.6 mmoles of base) of the reaction mixture was distilled to give a white solid (3.37 g.) b.p. 100-116°/10 mm. which, on examination by g.l.c. (2% NPGS, 130°; 10% SIL, 160°) was shown to contain durene and bromodurene. Preparative g.l.c. (7 ft. x 0.375 in. o.d. glass column containing 5% APL on celite at 225°) on the residue (1.66 g.) gave samples of 2,4,5,2',4',5'-hexamethylbibenzyl, bromo-2,4,5,2',4',5'-hexamethylbibenzyl, and dibromo-2,4,5,2',4',5'-hexamethylbibenzyl. These were identified from their mass spectra.

Mass spectra: see Appendix.

Measured portions of the reaction mixture were analysed by g.l.c. (2% NPGS, 95° for 3 mins. then programmed at 8°/min. to 155°, 135° for 8 mins. programmed at 16°/min. to 225°) using bromomesitylene and 3,5,3',5'-tetramethylbibenzyl as internal standards. The following compounds were detected:- durene (16.9 m/100 m.), 2,4,5,2',4',5'-hexamethylbibenzyl (2.69), bromo-2,4,5,2',4',5'-hexamethylbibenzyl (12.01), dibromo-2,4,5,2',4',5'-hexamethylbibenzyl (7.95). Bromodurene (18.2 mmoles) was consumed in the reaction and bromide ion (77.3 m/100 m.) was displaced.

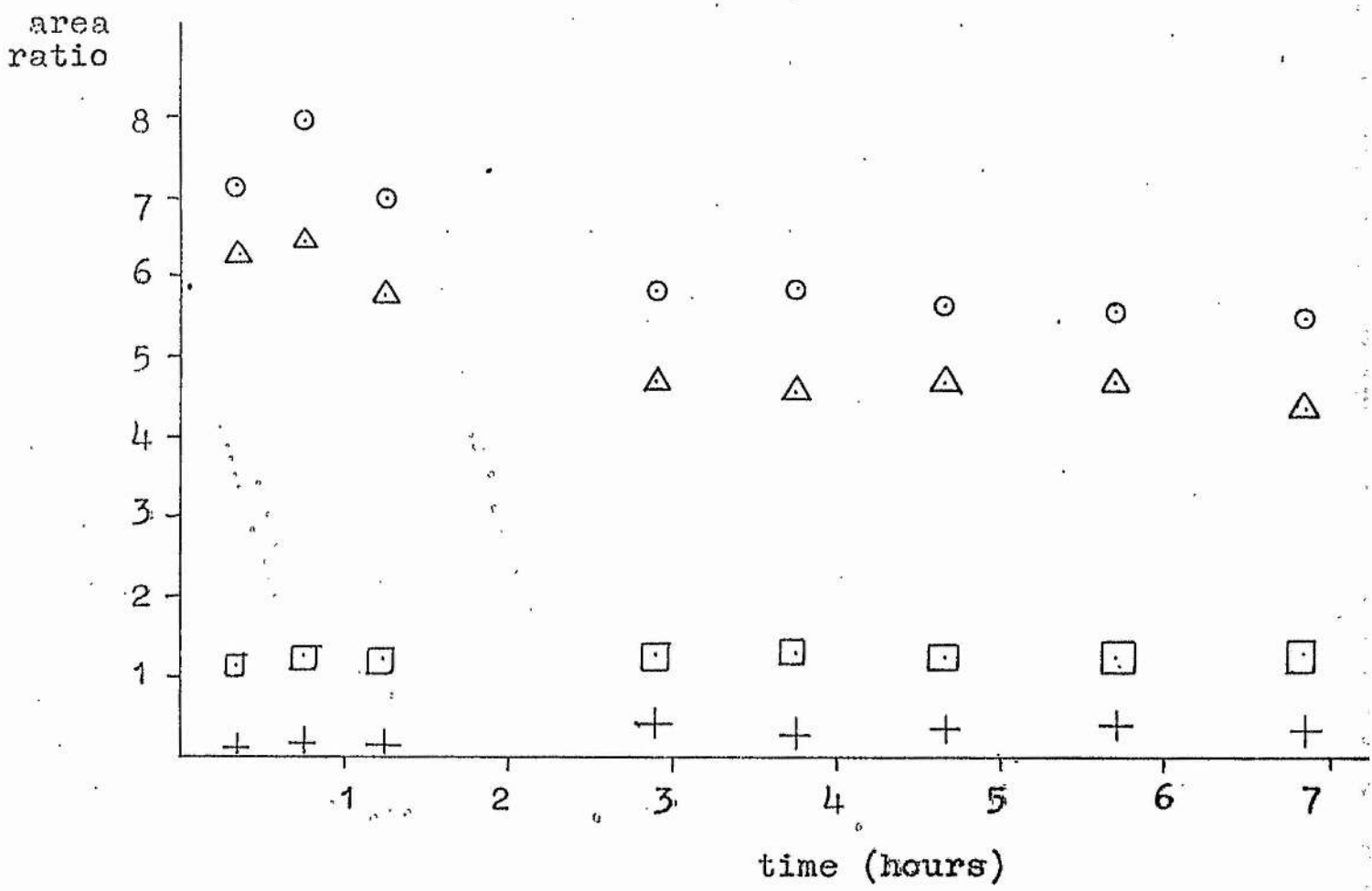
(k) Reaction of bromodurene with potassium t-butoxide:

1. Rate of formation of high-boiling products. Bromodurene (3.01 g., 14.1 mmoles) and potassium t-butoxide (0.61 g., 5.45 mmoles) were

Reaction of Bromodurene with

Potassium t-Butoxide

Rate of Formation of Products



○ bromobibenzyl/bibenzyl

△ dibromobibenzyl/bibenzyl

□ bromobibenzyl/dibromobibenzyl

\+ durene/bromodurene

allowed to react in an atmosphere of dry nitrogen, in a vessel heated to 220° on a constant temperature bath of boiling dodecane, and fitted with a rubber septum cap through which samples could be withdrawn with a fine glass pipette at intervals. Samples were analysed by g.l.c. (2% NPGS, 90° for 3 mins. programmed at 16°/min. to 150°; 105° for 3 mins. programmed at 32°/min. to 225°) and peak area ratios were plotted against time in the graph, page 80. .

Reaction of bromodurene with potassium t-butoxide: 2. Formation of low-boiling products. Bromodurene (9 g., 42.2 mmoles) and potassium t-butoxide (1.83 g., 16.3 mmoles) were allowed to react in a flask fitted with a condenser set up for distillation, and a trap immersed in liquid air. A slow stream of dry nitrogen was passed through the apparatus, and the temperature of the reaction flask was maintained at 220-240° for ten hours. A low-melting solid (0.90 g.) collected in the liquid air trap. The infra-red spectrum of this compound was identical to that of t-butanol (74.4 m/100 m.).

The product remaining in the reaction flask was dissolved in ether and washed with water. The ethereal solution was dried, and measured portions were withdrawn for analysis by g.l.c. (2% NPGS, 95° for 3 mins. programmed at 16°/min. to 150°; 135° for 8 mins. then programmed at 16°/min. to 225°) using bromomesitylene and 3,3',5,5'-tetramethylbibenzyl as internal standards. The following products were detected:- durene (21.7 m/100 m.), 2,4,5,2',4',5'-hexamethylbibenzyl (2.7), bromo-2,4,5,2',4',5'-hexamethylbibenzyl (10.7),

dibromo-2,4,5,2',4',5'-hexamethylbibenzyl (5.4).

Reaction of bromodurene and potassium t-butoxide: 3. In the presence of isomeric bromotrimethylbenzyl bromides. Bromodurene (15 g., 70.5 mmoles), potassium t-butoxide (3.0 g., 26.8 mmoles) and bromotrimethylbenzyl bromide (2.0 g., 6.9 mmoles) were allowed to react in the same way as in the previous experiment. The product collected in the liquid air trap (1.16 g.) was examined by infra-red spectroscopy (10% w/v solution in CCl_4, cell path-length 0.1 mm.) and had spectrum identical to that of t-butanol (58.8 m/100 m.).

The product mixture in the reaction flask was dissolved in ether and the solution poured into water. The layers were separated, and the aqueous layer was extracted with ether. The ethereal solution and extracts were combined and dried over magnesium sulphate and measured portions were withdrawn for analysis.

The bulk of the solution (24.0 mmoles of base) was distilled under vacuum to remove solvent, durene and bromodurene, and the residue (4 g.) was chromatographed on alumina. Elution with petroleum gave a white solid (1.0 g.). Examination by g.l.c. (2% NPGS, 150° for 3 mins., then programmed at 16°/min. to 225°) suggested that this contained a mixture of 2,4,5,2',4',5'-hexamethylbibenzyl, bromo-2,4,5,2',4',5'-hexamethylbibenzyl and dibromo-2,4,5,2',4',5'-hexamethylbibenzyl. Elution with a mixture of petroleum and benzene (5 : 1) gave a yellow oil (0.37 g.)

Examination by g.l.c. (2% NPGS, 150° for 3 mins. then programmed at 16°/min. to 225°) indicated that this contained three major components, A, B and C (retention time in min. and approximate peak area % given):- A (0.96, 20-25%), B (1.01, 25-30%), C (3.08, 40-50%). Preparative g.l.c. (7 ft. x 0.375 in. o.d. glass column containing 5% APL on celite at 175°) gave a sample containing a mixture of A and B, which was identified as a mixture of 2-bromo-3,4,6-trimethylbenzyl t-butyl ether and 3-bromo-2,4,5-trimethylbenzyl t-butyl ether.

N.m.r. (CCl_4): τ 3.01, 3.20 (two singlets, 1H, aromatic), 5.47, 5.71 (two singlets, 2H, benzyl), 7.55-7.82 (complex, 9H, aromatic methyl), 8.74 (singlet, 9H, t-butyl).

Mass spectrum: see Appendix.

Compound C was not isolated.

Elution with more polar solvents yielded only tars.

Measured portions of the reaction mixture were analysed by g.l.c. (2% NPGS, 95° for 3 mins., then programmed at 16°/min. to 150°; 135° for 8 mins., then programmed at 16°/min. to 225°) using bromomesitylene and 3,3',5,5'-tetramethylbibenzyl as internal standards. The following products were detected:- durene (24.6 m/100 m.), 2,4,5,2',4',5'-hexamethylbibenzyl (0.41), bromo-2,4,5,2',4',5'-hexamethylbibenzyl (4.76), dibromo-2,4,5,2',4',5'-hexamethylbibenzyl (7.55).

5. The Thermal Decomposition of Sodium o-Halophenolates

(a) Thermal decomposition of sodium o-bromophenolate in dodecane. Sodium o-bromophenolate (2.6 g., 13.5 mmoles) was allowed to decompose in dodecane (15 ml.), heated to reflux temperature, for three days, in an atmosphere of dry nitrogen. The reaction mixture was filtered to give a grey amorphous solid (1.04 g.) which was insoluble in water, benzene, ethanol, acetone and ether.

The filtrate was washed with water and dried over magnesium sulphate. Dodecane was removed under vacuum, and the residue was distilled to give diphenylene dioxide (0.05 g., 2.1 m/100 m. of phenolate) b.p. 98-102°/0.5 mm. On recrystallisation from petroleum this had m.p. 118° (lit.,[101] 120-121°).

N.m.r. (CCl_4): τ 3.24 singlet.

(b) Thermal decomposition of sodium o-bromophenolate in mesitylene. Sodium o-bromophenolate (2.0 g., 10.3 mmoles) in mesitylene (25 ml.) was allowed to decompose in an autoclave at 250° for five days in an atmosphere of dry nitrogen. The product was washed with water, dried over magnesium sulphate, and mesitylene was removed under vacuum. The residue was distilled to give diphenylene dioxide (0.35 g., 37 m/100 m. of phenolate) b.p. 100-110°/0.05 mm., which on recrystallisation from petroleum had m.p. 118°, and on mixing with diphenylene dioxide from (a) had m.p. 118°. The residue (0.5 g.)

from this distillation was chromatographed on alumina but only tars were obtained. Bromide ion (70 m/100 m. of phenolate) was determined gravimetrically.

(c) Thermal decomposition of sodium o-bromophenolate in t-butylbenzene, in the presence of trans-stilbene. Sodium o-bromophenolate (5.15 g., 26.0 mmoles) in t-butylbenzene (65 ml.) containing trans-stilbene (11.0 g., 61 mmoles), was allowed to decompose as described in (b). The product was dissolved in ether and washed with water, the ethereal solution was dried over magnesium sulphate, and ether and t-butylbenzene were removed under vacuum. The residue was distilled to give stilbene (10.5 g.) b.p. 82-92°/0.05 mm. and diphenylene dioxide (0.74 g., 30.0 m/100 m. of phenolate) b.p. 98-108°/0.05 mm. On recrystallisation from petroleum this had m.p. 118° and on mixing with diphenylene dioxide from (a) m.p. 118°. The residue (0.6 g.) from the distillation was chromatographed on alumina but only tars were obtained. Bromide ion (70 m/100 m. of phenolate) was determined gravimetrically.

(d) Thermal decomposition of sodium pentachlorophenolate in mesitylene. Sodium pentachlorophenolate (10 g., 35 mmoles) in mesitylene (65 ml.) was allowed to decompose as described in experiment (b). The product was dissolved in ether and washed with water acidified with dilute nitric acid. The ethereal solution

was dried over magnesium sulphate, and ether and mesitylene were removed under vacuum. The residue was distilled to give a yellow solid (8.0 g.) b.p. 100-140°/0.1 mm. which was chromatographed on silica (300 g.). Elution with petroleum gave 2,3',4,5',6-pentamethyldiphenylmethane (2.53 g., 30 m/100 m. of phenolate) which was recrystallised from ethanol m.p. 67-68° (lit.,[102] 67°). N.m.r. (see Table II, page 93) and mass spectrum (see Appendix) confirm this structure.

Elution with petroleum/benzene (5 : 1) gave a white oily solid 1.68 g.), more polar solvents yielded tars only. The solid was chromatographed on alumina; elution with petroleum and benzene gave a viscous yellow oil (0.1 g.) which was not purified further. Elution with methanol gave tetrachlorophenol (0.89 g., 3.84 mmoles, 10.95 m/100 m. of phenolate) which was recrystallised from light petroleum (b.p. 60-80°) m.p. 106-107°.

N.m.r. ($CDCl_3$): τ 2.80 (singlet, 1H, Ph), 4.29 (singlet, 1H, OH).

I.r. (Nujol): 3580, 3530, 3490, 1550, 1290, 1215, 960, 850, 700 $cm.^{-1}$

It was identified as 2,3,5,6-tetrachlorophenol by comparison with authentic samples by g.l.c. (2% NPGS, 175° for 5 mins., programmed at 16°/min. to 225°).

The residue from the distillation (5.4 g.) was chromatographed on alumina but only tars were obtained. Chloride ion (131 m/100 m.

of phenolate) was determined gravimetrically.

(e) Thermal decomposition of sodium pentachlorophenolate in t-butylbenzene. Sodium pentachlorophenolate (10 g., 35.1 mmoles) in t-butylbenzene (60 ml.) was allowed to decompose as described in experiment (b). The product was dissolved in ether and extracted with dilute sodium hydroxide (0.2M). The ether solution was dried over magnesium sulphate, ether and t-butylbenzene were removed under vacuum, and the residue was recrystallised from 1,2,4-trichlorobenzene to give octachlorodiphenylene dioxide (0.12 g., 0.26 mmoles, 0.74 m/100 m. of phenolate) m.p. 334-335°, mixed with an authentic sample m.p. 334-335°; the i.r. spectrum was indistinguishable from that of an authentic sample.

The basic extract was just acidified with dilute nitric acid (2M) and extracted with ether. The ethereal solution was dried over magnesium sulphate and evaporated to give pentachlorophenol (6.9 g.). The i.r. spectrum was indistinguishable from that of an authentic sample. Chloride ion (42.7 m/100 m. of phenolate) was displaced.

(f) Thermal decomposition of sodium pentachlorophenolate in t-butylbenzene and p-xylene. Sodium pentachlorophenolate (10 g., 35.1 mmoles) in t-butylbenzene (35 ml., 225 mmoles) and p-xylene (28 ml., 225 mmoles) was allowed to decompose as described in

experiment B. The product was dissolved in ether and extracted with dilute sodium hydroxide (0.2M). The ether solution was dried over magnesium sulphate and a portion was withdrawn for analysis. Solvent was removed from the bulk of the solution and the residue was distilled to give two fractions: (i) a colourless liquid (1.54 g.) b.p. 88-98°/0.05 mm.; (ii) a colourless liquid (1.04 g.) b.p. 120-130°/0.05 mm. Examination of both fractions by g.l.c. (2% NPGS, 160°) showed that they contained a mixture of two compounds. The fractions were combined and purified by preparative g.l.c. (15 ft. x 0.375 in. o.d. glass column containing 10% APL on celite at 200°) to give samples of 2,4',5-trimethyldiphenylmethane (n.m.r.: see Table II, page 93; mass spectrum: see Appendix), and 4-methyl -t-butyldiphenylmethane (n.m.r.: see Table II, page 93). (Found: C, 90.4; H, 9.55. $C_{17}H_{22}$ requires C, 90.2; H, 9.8%.)

The residue from the distillation (1.7 g.) was chromatographed on alumina, but only tars were obtained.

The basic extract was acidified with dilute nitric acid (2M) and extracted with ether. The ether solution was dried over magnesium sulphate, a measured portion was withdrawn for analysis, and ether was removed from the remainder under vacuum. Preparative g.l.c. (7 ft. x 0.375 in. o.d. glass column containing 10% PEGA on celite at 180° for 45 mins. then programmed at 24°/min. to 200°) gave samples of three compounds:- (i) a white solid which was

sublimed, block temperature 85°/10 mm. This was identified as 2,3,5-trichlorophenol from its n.m.r. and mass spectra:

N.m.r. (CCl_4): τ 2.94, 3.05 (two doublets, J=2.4 c/s, 2H, aromatic), 4.25 (broad singlet, 1H, OH).

Mass spectrum: see Appendix.

I.r. (20% w/v solution in CCl_4, 0.1 mm. silver chloride cell):
3530, 3090, 1450, 1300, 1220, 1170, 1105, 1055, 955, 700 $cm.^{-1}$

(ii) 2,3,5,6-tetrachlorophenol which was sublimed, block temperature 125°/10 mm., m.p. 97-98°:

N.m.r. (CD_3COCD_3 20% w/v solution): τ 2.70 (broad singlet).

I.r. (20% w/v solution in $CHCl_3$ 0.1 mm. silver chloride cell):
3510, 2580, 1550, 1285, 960 $cm.^{-1}$

Mass spectrum: see Appendix.

(iii) an oil:

N.m.r. (CCl_4): τ 2.89 (triplet, J = 6 c/s, 1H), 3.10 (triplet, J = 1.6 c/s, 2H), 3.29 (doublet, J = 1.4 c/s, 3H).

Mass spectrum: see Appendix.

The mass spectrum suggested that tetrachlorophenol was present in this sample.

Measured portions of the product mixtures were analysed by g.l.c. (10% APL, 195° and 2% NPGS, 179° for 5 mins., programmed at 16°/min. to 225°) using biphenyl and 2,4,5,2',4',5'-hexamethylbibenzyl as internal standards. The following products were detected:-

2,4',5-trimethyldiphenylmethane (25.5 m/100 m. of phenolate), 4-methyl-4'-t-butyldiphenylmethane (5.2), trichlorophenol (10.0), 2,3,5,6-tetrachlorophenol (8.42), 2,3,4,5-tetrachlorophenol (3.54). Chloride ion (143.5 m/100 m.) was displaced.

(g) 1. Thermal decomposition of sodium pentachlorophenolate in p-xylene. Sodium pentachlorophenolate (10 g., 35 mmoles) in p-xylene (60 ml.) was allowed to decompose as described in (b). The product was dissolved in ether and extracted with dilute sodium hydroxide (0.2M). The ethereal solution was dried over magnesium sulphate and a portion was withdrawn for analysis; ether and p-xylene were removed from the bulk of the solution under vacuum and the residue was distilled to give 2,4',5-trimethyldiphenylmethane (2.50 g.) b.p. 82-84°/0.05 mm.

N.m.r.: see Table II, page 93.

Mass spectrum: see Appendix.

The residue from the distillation (8 g.) was chromatographed on alumina, but only tars were obtained.

The basic extract was acidified with dilute nitric acid (2M) and extracted with ether. The ether solution was dried over magnesium sulphate, and a portion was withdrawn for analysis.

By g.l.c. analysis (10% APL, 200° and 2% NPGS, 179° for 5 mins. then programmed at 16°/min. to 225°) on measured portions of the product mixtures using diphenyl and 2,4,5,2',4',5'-hexamethylbibenzyl

as internal standards, the following products were detected:- 2,4',5-trimethyldiphenylmethane (36.8 m/100 m. of phenolate), 2,3,5,6-tetrachlorophenol (8.05), 2,3,4,5-tetrachlorophenol (10.55). Chloride ion (135 m/100 m.) was displaced.

2.Thermal decomposition of sodium pentachlorophenolate in p-xylene in a sealed glass tube. Sodium pentachlorophenolate (2 g., 6.9 mmoles) in p-xylene (10 ml.) was allowed to decompose in a sealed glass tube contained in an autoclave under the conditions described in experiment (b). The product was dissolved in ether and extracted with dilute sodium hydroxide (0.2M). The ether solution was dried over magnesium sulphate and a portion was withdrawn for analysis. The basic extract was acidified and extracted with ether, and the ethereal extract was dried over magnesium sulphate.

Measured portions of the product mixtures were analysed by g.l.c. (10% APL 200°, 2% NPGS 179° for 5 mins., then programmed at 16°/min. to 225°) using diphenyl and 2,4,5,2',4',5'-hexamethylbibenzyl as internal standards. The following products were detected:- 2,4',5-trimethyldiphenylmethane (18.6 m/100 m. of phenolate), trichlorophenol (23.15), 2,3,5,6-tetrachlorophenol (2.85). Chloride ion (133 m/100 m.) was displaced.

(h) Thermal decomposition of sodium pentachlorophenolate in durene. Sodium pentachlorophenolate (5 g., 17.5 mmoles) in durene (20 g.) was allowed to decompose as described in experiment (b). The product was dissolved in ether, and extracted with dilute sodium hydroxide (0.2M). The ethereal solution was dried over magnesium sulphate, a measured portion was withdrawn for analysis, and ether and durene were removed from the remainder under vacuum. The residue was distilled to give 2,2',3,4',5,5',6-heptamethyldiphenylmethane (1.05 g.) b.p. 130-135°/0.2 mm., which on recrystallisation from petroleum had m.p. 146°. (Found: C, 90.1; H, 10.0. $C_{20}H_{26}$ requires C, 90.2; H, 9.8%.)

N.m.r.: see Table II, page 93.

The residue from the distillation (2 g.) was chromatographed on alumina, but tars only were obtained.

The basic extract was acidified with dilute nitric acid (2M) and extracted with ether. The ethereal solution was dried over magnesium sulphate, and measured portions were withdrawn for analysis.

Measured portions of the product mixtures were analysed by g.l.c. (2% NPGS, 175°; 179° for 5 mins. programmed at 16°/min. to 225°) using phenylbenzoate and 2,4,5,2',4',5'-hexamethylbibenzyl as internal standards. The following products were detected:- 2,2',3,4',5,5',6-heptamethyldiphenylmethane (24.5 m/100 m. phenolate), trichlorophenol (7.1), 2,3,5,6-tetrachlorophenol (3.68),

2,3,4,5-tetrachlorophenol (2.38). Chloride ion (165 m/100 m.) was displaced.

TABLE II: H' N.m.r. Spectral Data for Diphenylmethanes (τ values)

	Substituents	Aromatic[a]	Methylene[b]	Alkyl[c]
1.	2,4',5-Me	3.09	6.22	7.67-7.92
2.	2,3',4,5',6-Me	3.20-3.60	6.15	7.65-7.91
3.	2,2',3,4',5,5',6-Me	3.05, 3.70	6.13	7.55-8.08
4.	4-Me, 4'-Bu^t	2.86, 2.99	6.17	7.73, 8.72

Solvent: CCl_4 (spectra 1,2,4); $CDCl_3$ (spectrum 3).

(a) singlet (1); complex (2); two singlets (3); τ 2.86 centre of A_2B_2 system, τ 2.99 singlet (4).

(b) 2H, singlet.

(c) complex (1, 2, 3); τ 7.73 singlet, methyl, τ 8.72 singlet, t-butyl (4).

APPENDIX OF MASS SPECTRAL DATA

Bibenzyls

Iodo-2,4,5,2',4',5'-hexamethylbibenzyl

Ion (m/e):	393	392	259	134	133	117	115	91
Abundance %:	5	20.7	25.9	12.9	100	8.4	4.7	6.1

Diiodo-2,4,5,2',4',5'-hexamethylbibenzyl

Ion (m/e);	518	265	260	259	249	234	133	132	131	117	115
Abundance %:	13	9.5	11.8	100	6.8	5.2	10.1	4.9	5.7	13.5	6.8
Ion (m/e);	91	76	61	60	58	57	56	55	43	42	41
Abundance %:	12.9	26.7	15.3	7.1	5.1	96	53.4	12.7	85	55	60

Dibromohexamethylbibenzyl Isomers from Bromoisodurene

Ion (m/e):	426	424	422	224	215	214	213	212	169	168	167
Abundance %:	13	24.1	11.1	13	13	100	16.7	100	16.6	11	42.6
Ion (m/e);	133	117	116	115	91						
Abundance %:	42.4	18.5	7.0	14.8	17.6						

Bromooctamethylbibenzyl Isomers

Ion (m/e):	374	372	294	280	265	227	225	160	148	147	146
Abundance %:	11	11	8.4	10.8	7	17.1	17.1	20.2	16.8	100	32.3
Ion (m/e):	133	132	131	117	115	105	91	82	80		
Abundance %:	28.9	18.1	11.3	9.5	7.8	8	13.2	7.8	8.1		

Samples from Reaction of Bromodurene with Sodamide :-

2,4,5,2',4',5'-hexamethylbibenzyl

Ion (m/e):	268	267	266	265	251	146	134	133	132	131	117
Abundance %:	10.3	98	100	10	11.8	14.7	91.4	99.1	33.8	11.8	11.8
Ion (m/e):	115	105	91	79	77						
Abundance %:	7.4	10.3	29.4	10.3	20.6						

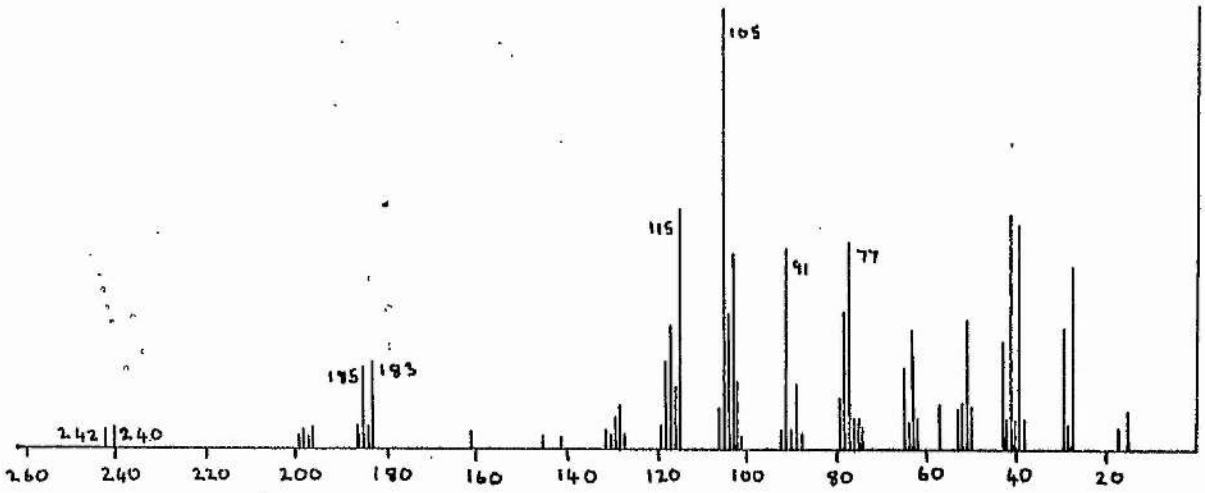
Bromo-2,4,5,2',4',5'-hexamethylbibenzyl

Ion (m/e):	347	346	345	344	265	213	211	134	133	132	131
Abundance %:	10.2	47.0	10.2	47.0	14.0	42.6	42.6	39.8	100	14.7	10.4
Ion (m/e):	117	116	115	105	91	77					
Abundance %:	26.5	11.8	19.1	11.0	25.0	9.5					

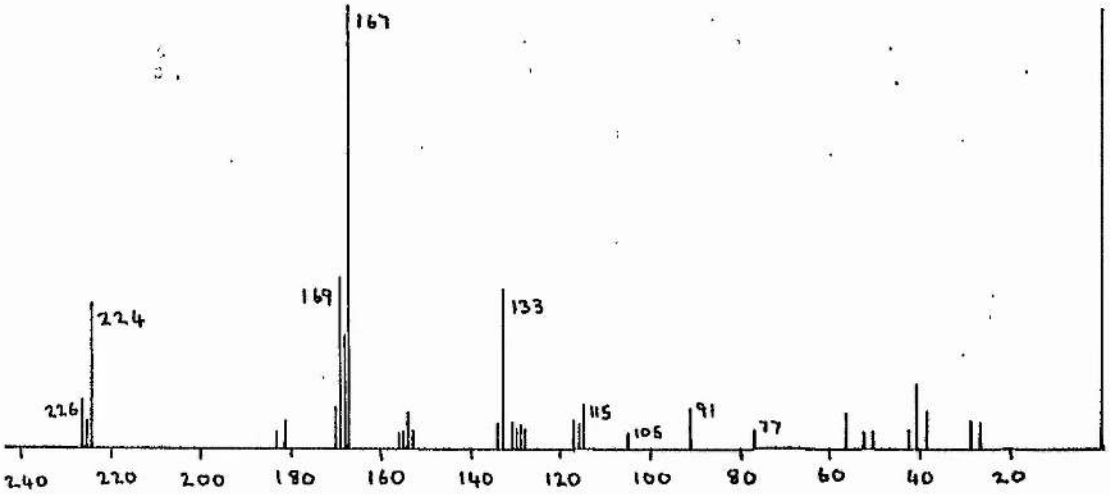
Dibromo-2,4,5,2',4',5'-hexamethylbibenzyl

Ion (m/e):	424	422	420	265	214	213	212	211	133	131
Abundance %:	11.8	23.6	13.2	9.6	14.7	100	18.4	100	17.7	8.8
Ion (m/e):	117	116	115	91						
Abundance %:	19.1	9.5	13.2	16.2						

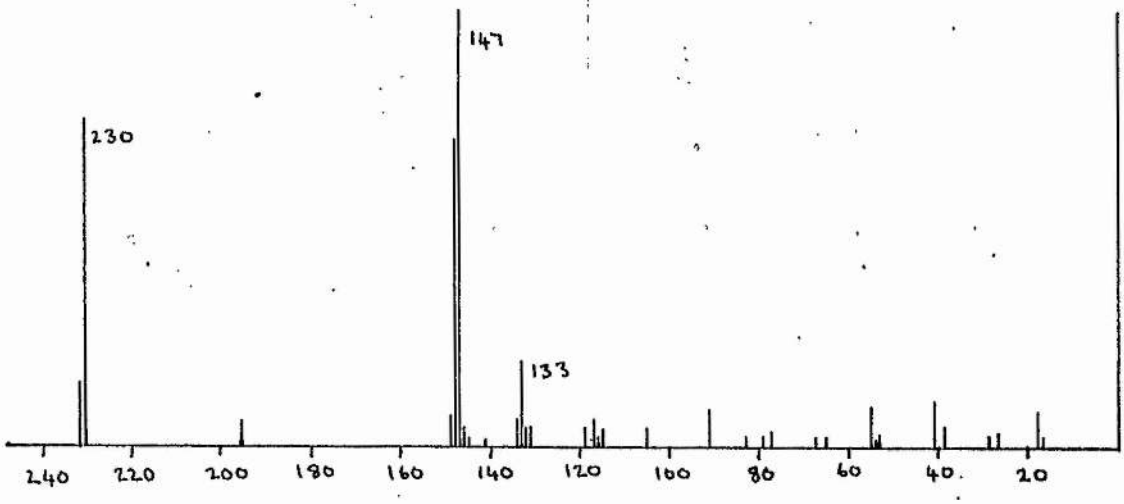
Halomethylisopentylbenzenes.



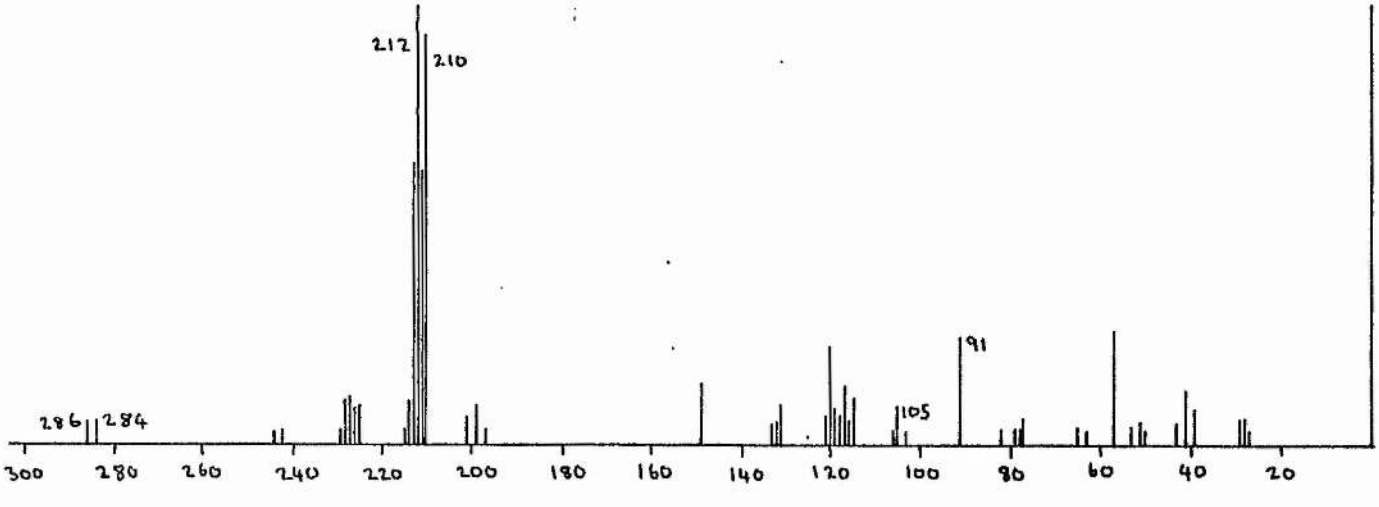
2-Bromo-3-methylisopentylbemzene



Chlorotrimethylisopentylbenzeme Isomers

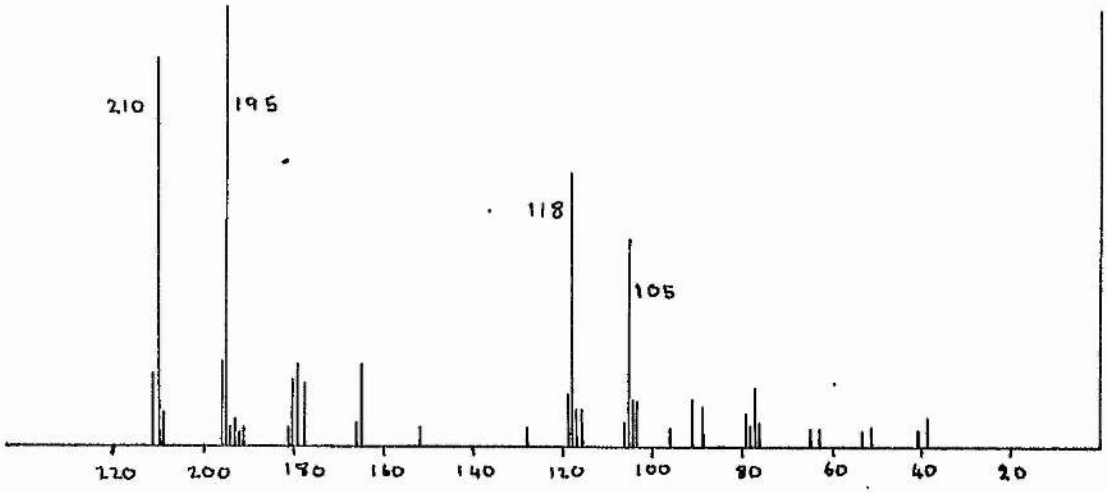


(Tetramethylphenyl)cyclohexylmethane

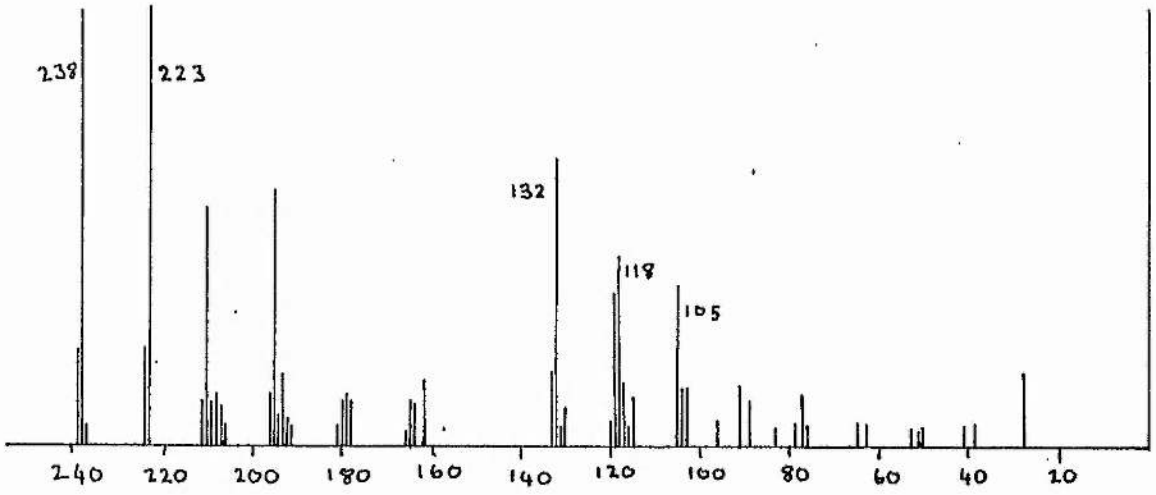


Trimethylbenzyl t-Butyl Ether

Diphenylmethanes

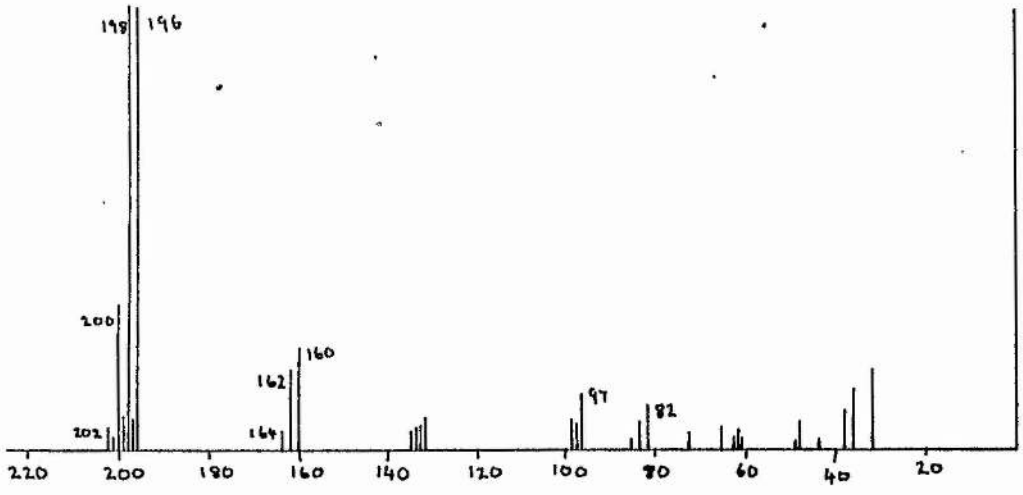


2,4',5-Trimethyldiphenylmethane.

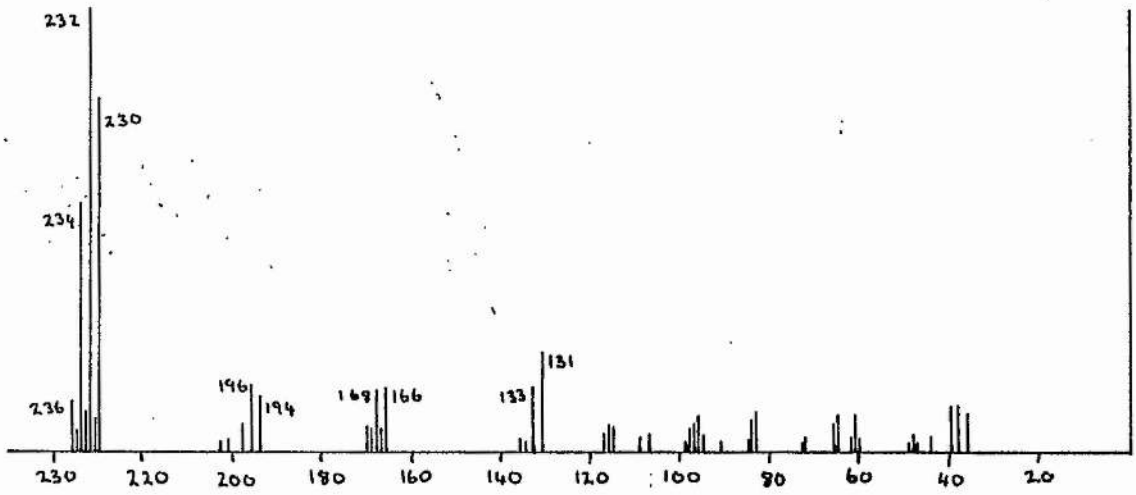


2,3',4,5',6-Pentamethyldiphenylmethane.

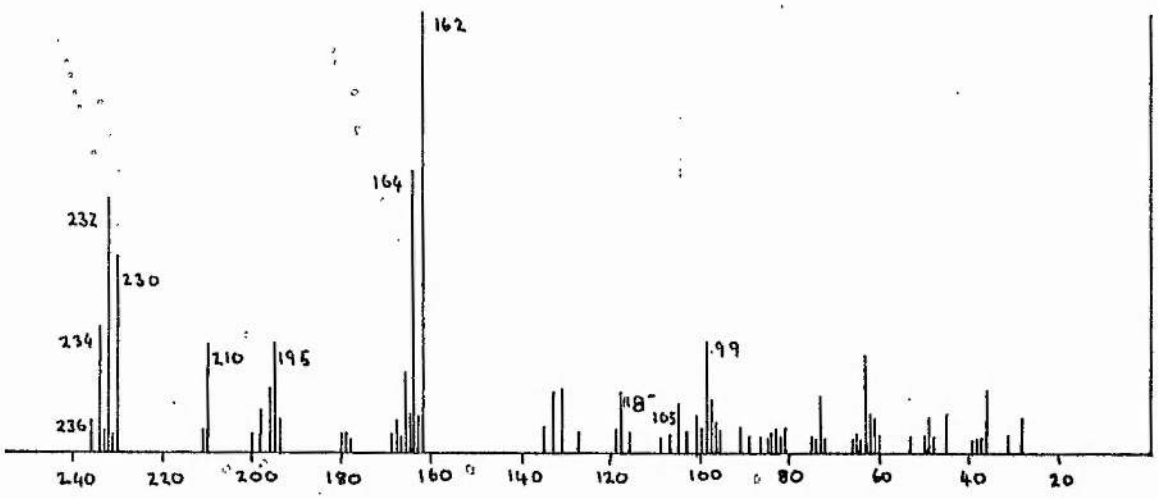
Chlorophenols.



2,3,5-Trichlorophenol



Tetrachlorophenol



Sample Containing Tetrachlorophenol Isolated from the Thermal Decomposition of Sodium Pentachlorophenate in t-Butylbenzene and p-Xylene.

DISCUSSION

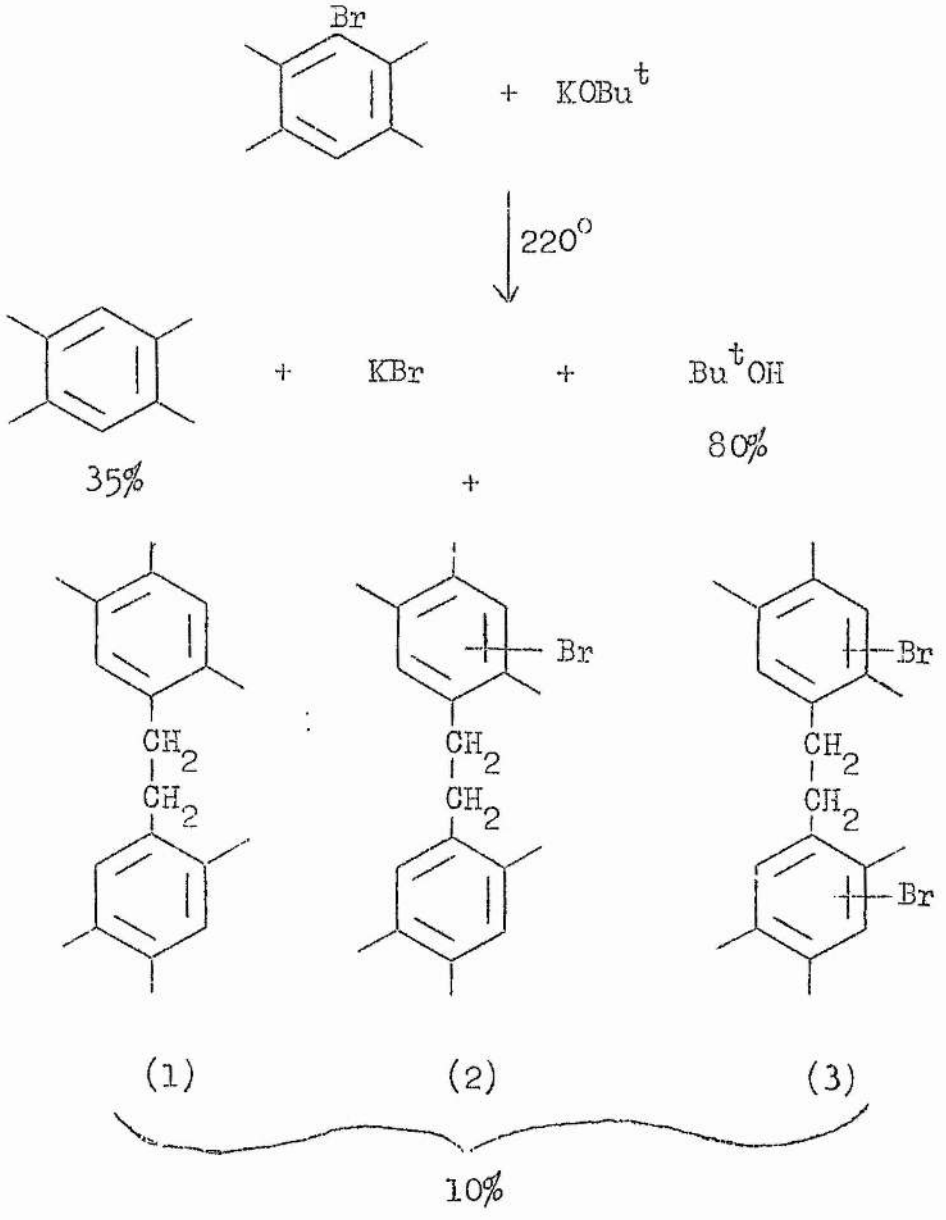
-oOo-

As described in the Introduction, bases such as sodamide do not react with aryl halides to give arynes when both ortho positions are blocked. The starting point of this investigation was the observation that bromodurene eliminated hydrogen bromide on reaction with potassium t-butoxide at high temperatures. The mechanism of this reaction was obviously of interest, raising, for example, the possible participation of 1,4-dehydrobenzenes.

1. The Reaction of Bromodurene with Base

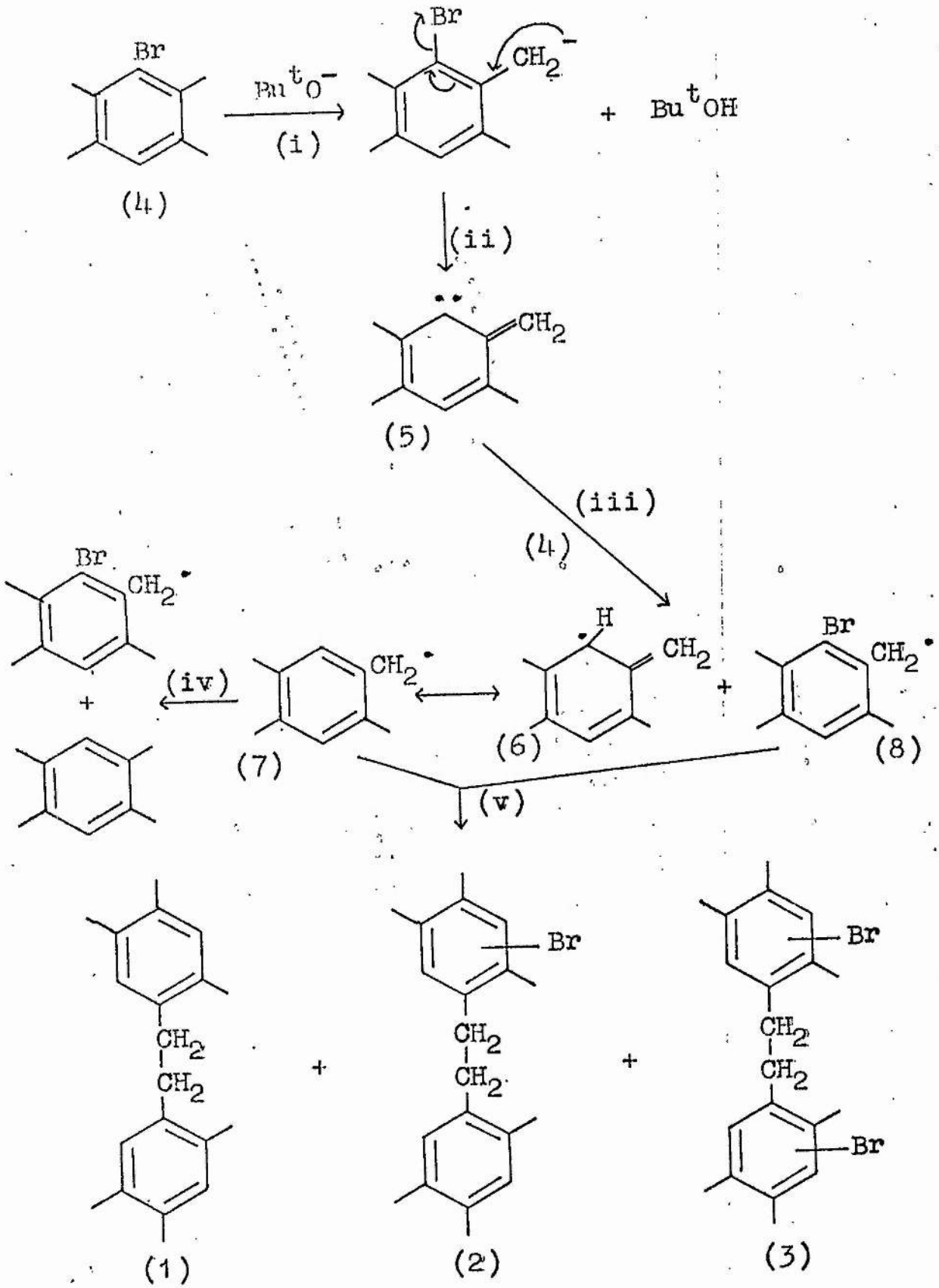
The reaction of bromodurene with potassium t-butoxide was found to give durene as the major product. Higher boiling compounds were

also formed which were identified as the bibenzyls (1), (2) and (3). These results are summarised below.

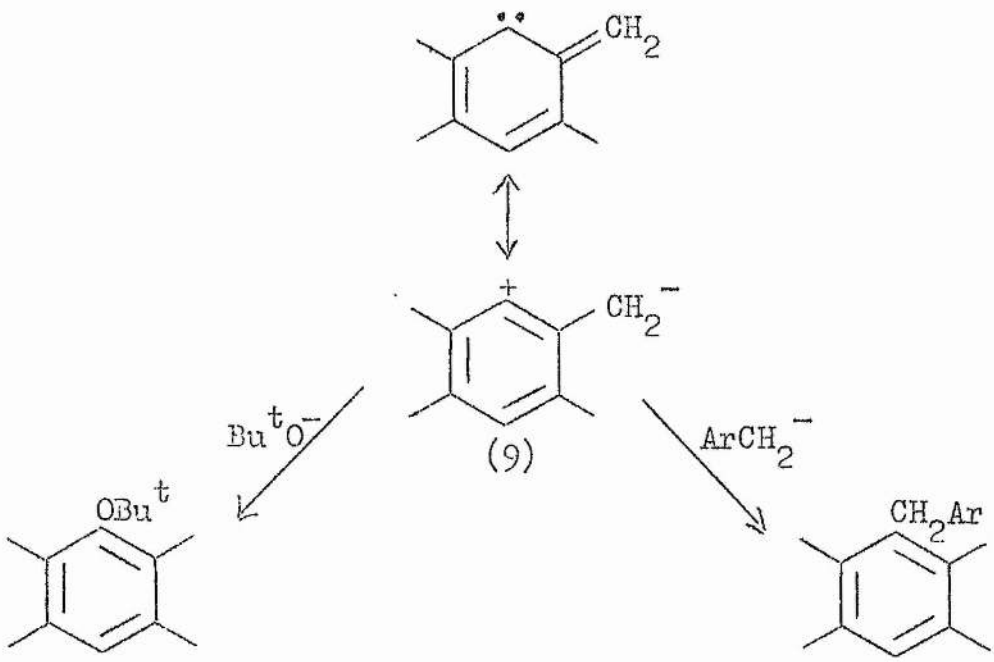


The presence of bibenzyls among the products suggests the participation of benzyl radicals in the reaction. A possible

Scheme I

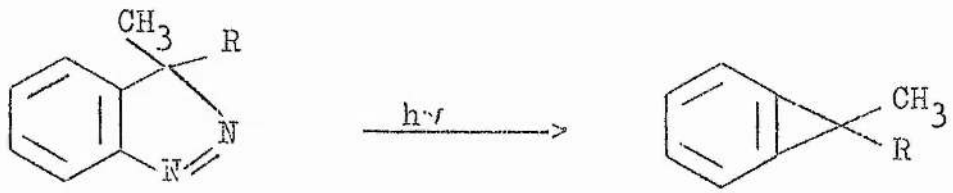

Br
Bu^tO^-
(i)
Br
CH_2^-
+ Bu^tOH
(4)
(ii)
CH_2
(5)
(iii)
(4)
Br
$CH_2^{\bullet}$
(iv)
+
$CH_2^{\bullet}$
H
CH_2
(7)
(6)
Br
$CH_2^{\bullet}$
(8)
(v)
CH_2
CH_2
(1)
+
Br
CH_2
CH_2
(2)
+
Br
CH_2
CH_2
Br
(3)

reaction scheme involving such intermediates is outlined in Scheme I. In this scheme the initial step, i, in the reaction is metallation by the base to give a benzyl anion, followed by loss of bromide ion, step ii, to give the carbene (5). Such intermediates may have either a triplet or a singlet structure. However if a singlet carbene structure is involved then one might expect aryl t-butyl ethers or diphenylmethanes to be formed by reaction of the dipolar resonance form (9) with other anions in the system. Such products were not isolated or detected in reactions with bromodurene.

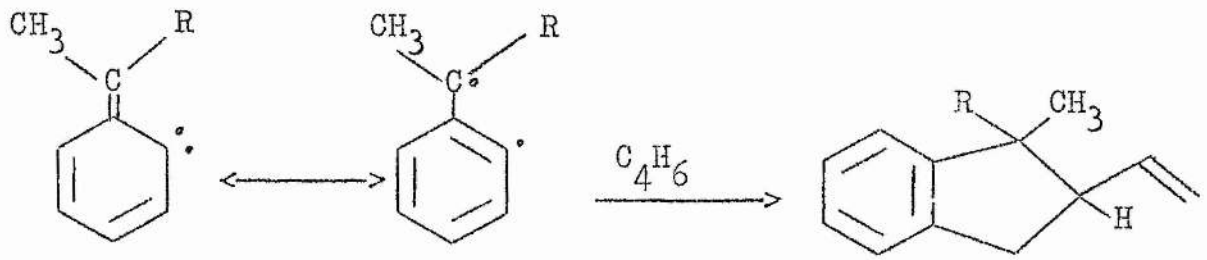


A precedent for a triplet carbene structure is provided by Closs and his co-workers[103] in the photolysis of 3H-indazoles to

benzocyclopropenes:



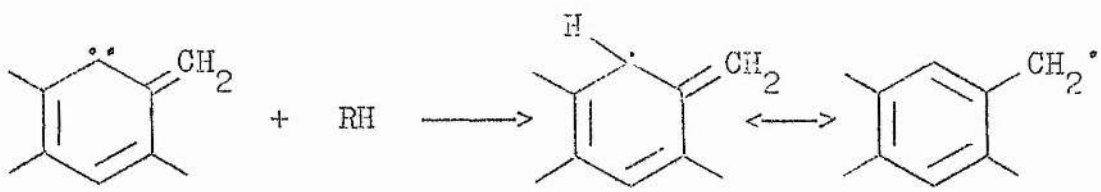
He obtained e.s.r. spectra strongly suggestive of a triplet intermediate, and he postulated resonance with the diradical (10) which he was able to trap with butadiene:



(10) (2 isomers)

Closs was unable to obtain corresponding addition products with simple olefins, and he therefore postulated a two-step mechanism for the addition to butadiene, involving a second, resonance-stabilised, diradical. A similar explanation could account for the absence of addition products when bromodurene and potassium t-butoxide were allowed to react in cyclohexene in this investigation.

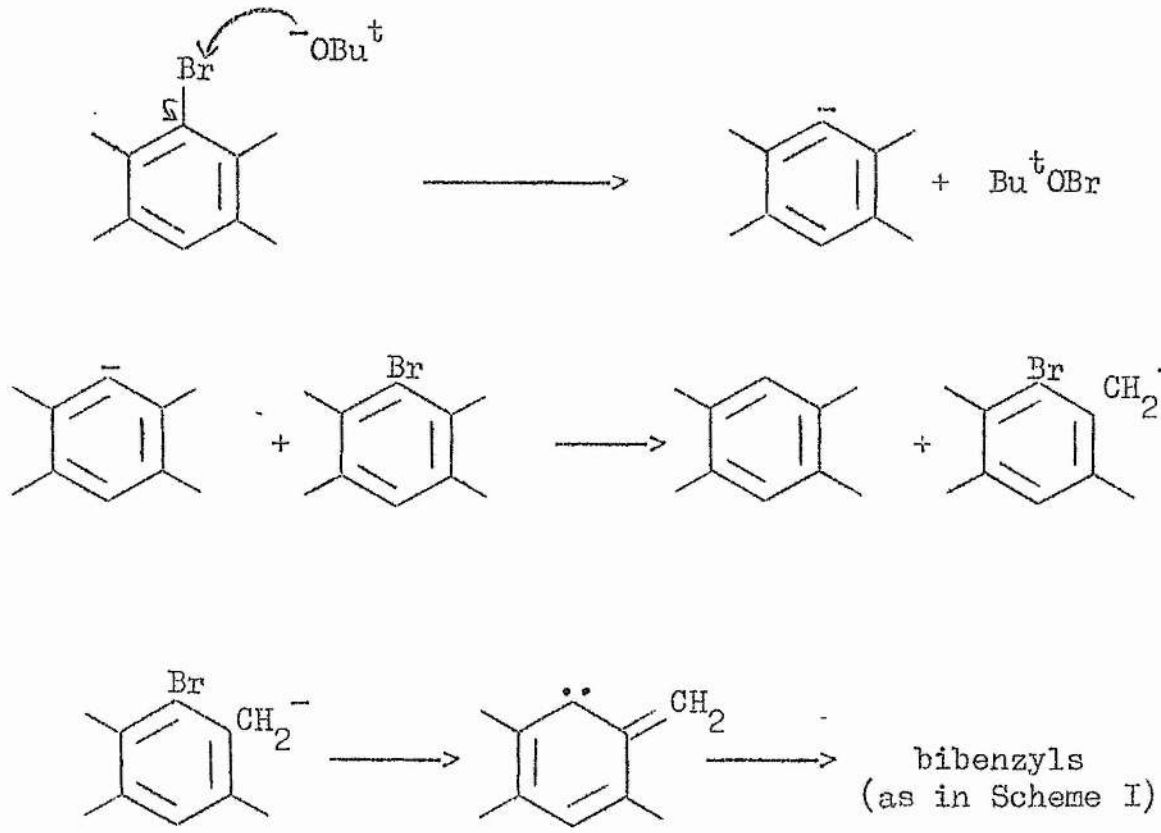
Closs's experiments were carried out photolytically, however, and under such conditions a diradical might be more feasible than under the thermal conditions of the experiments described in this thesis. An alternative, and perhaps more acceptable, mechanism involves reaction of the carbene, in the triplet state, with another molecule of bromodurene, to give a benzyl radical directly, as was formulated in Scheme I.



This is then assumed to react by dimerisation or cross-coupling to give the observed products.

In Scheme I, durene is assumed to arise by the transfer of hydrogen from bromodurene to the benzyl radical (7), step iv. Although transfers of this type between benzyl radicals and chlorotoluene occur to the extent of about 15% at 170°,[79] as discussed in the Introduction, and the high temperatures at which the reaction with bromodurene is carried out would favour the transfer reaction, it seems doubtful whether all the durene formed could arise by this means.

An alternative route to durene is therefore postulated in Scheme II, involving nucleophilic attack on bromine by the base, paralleling Bunnett's observations on the deiodination of iodobenzenes by potassium t-butoxide in dimethyl sulphoxide.[50]



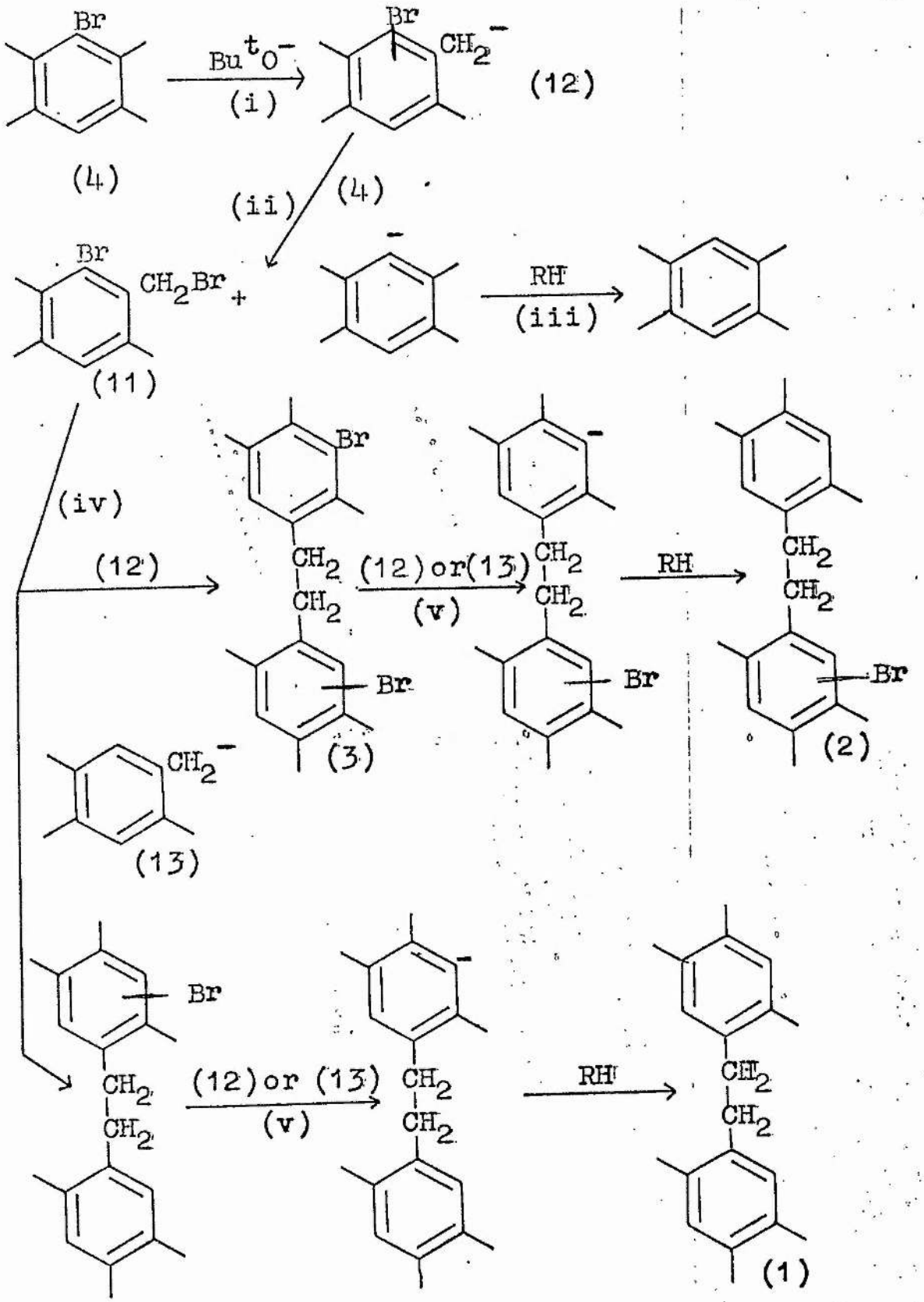
Scheme II

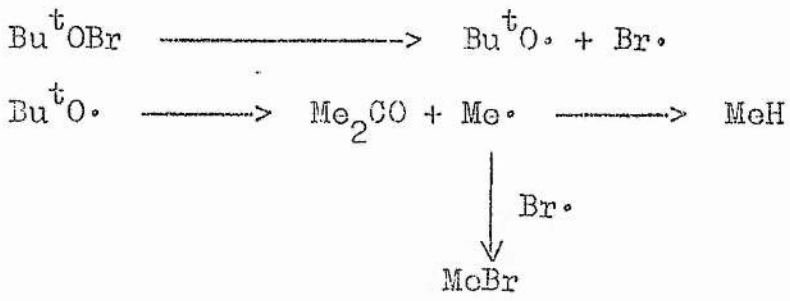
Support for the formation of durene by this route in preference to that outlined in Scheme I is obtained from the reaction of bromodurene with sodamide. Under the same conditions as those used in the reaction of bromodurene with potassium t-butoxide, the

yield of durene is reduced to 16 m/100 m. of base, approximately half that obtained with potassium t-butoxide, while the yield of bibenzyls is increased slightly. It is reasonable to expect a difference in reactivity between t-butoxide ion and amide ion in nucleophilic attack on the halogen, thus leading to differences in the yield of durene. On the other hand, since the formation of phenyl anions from aryl halides and sodamide is known to occur under conditions in which no reaction occurs between bromodurene and sodamide,[17] and since the removal of an α proton by lithium cyclohexylamide from toluene is found to be about one hundred times faster than the removal of a proton from the aromatic ring,[104] the formation of the benzyl anion is presumably not rate-determining, and differences in the basicity of t-butoxide and amide ions will not affect the products formed from it.

A serious objection to Scheme II, however, is the absence of identifiable products assignable to the precursory t-butyl hypobromite, which should be formed to the extent of 35 m/100 m. The only low-boiling product isolated in reaction of bromodurene with potassium t-butoxide was t-butanol (74 m/100 m.). Acetone, which might be expected to arise from the decomposition of t-butyl hypobromite, was absent (g.l.c.), and other possible decomposition products such as methane or methyl bromide were not detected either.

Scheme III


Br
Bu^tO^-
(i)
CH_2^-
(12)
(4)
(ii)
(4)
Br
CH_2Br^+
(11)
RH
(iii)
(iv)
(12)
Br
CH_2
CH_2
(12) or (13)
(v)
RH
Br
(3)
(2)
CH_2^-
(13)
Br
CH_2
CH_2
(12) or (13)
(v)
RH
(1)



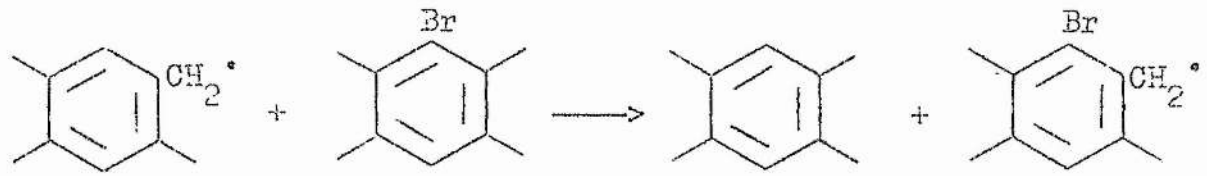
If t-butyl hypobromite is formed, and decomposes via a radical path, these radicals might act as a precursor to the bibenzyls, rather than the triplet carbene intermediate.

Although the appearance of bibenzyls among the products suggests the participation of radicals in the reaction, their occurrence can be explained by a mechanism not involving radicals, as in Scheme III. This scheme also involves nucleophilic attack on bromine, in this case by the benzyl anion, step ii, again recalling the dehalogenation of trihalobenzenes by potassium t-butoxide in dimethyl sulphoxide reported by Bunnett and Victor.[50]

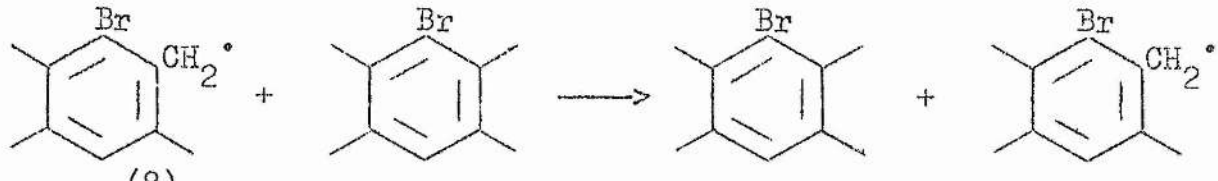
The formation of bibenzyls is attributed to the reaction of benzyl bromide, formed by nucleophilic attack of a benzyl anion on bromodurene, with a benzyl anion. Coupling between benzyl halides and benzyl anions is well known, as for example in the formation of bibenzyl in the reaction of triphenylsilylpotassium with benzyl chloride.[105] The monobromohexamethylbibenzyl (2) and hexamethylbibenzyl (1) could either arise from attack on benzyl bromide by the benzyl anion (13) derived from the durene formed during the

reaction, step iv, or by debromination of dibromohexamethylbibenzyl (3), step v. This implies that the dibrominated bibenzyl (3) will be formed initially to a greater extent than the other two, and as the concentrations of durene and of (3) increase the concentrations of (1) and (2) relative to (3) will also increase. When samples, taken during the course of a reaction, were examined, the concentrations of (1) and (2) relative to (3) were indeed found to increase with time, but the increase in the ratio of (2) : (3) was very slight, and possibly not significant.

It is not immediately easy to reconcile this result with the radical mechanisms of Schemes I and II since the formation of the brominated benzyl radical (8) is accompanied by the formation of a non-brominated radical (7). However at the high temperature at which this reaction takes place, the radical transfer reactions shown below should occur, at least to the extent of about 15%.[79]

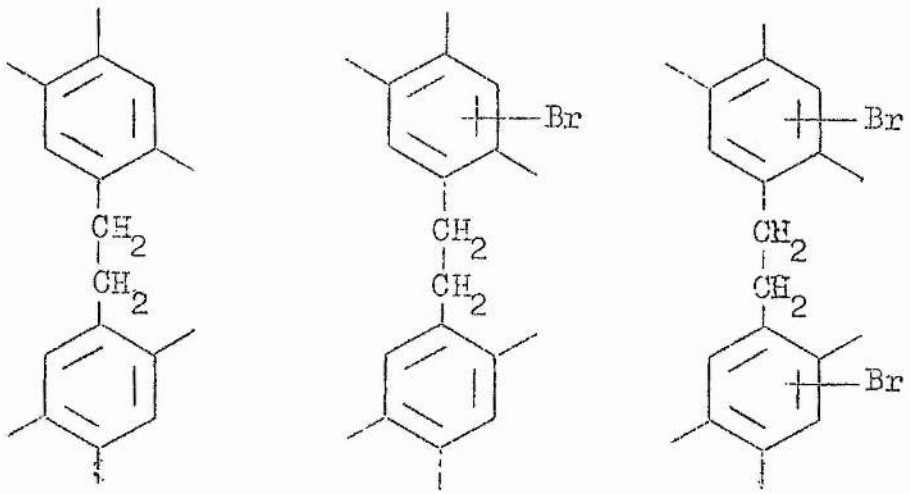


(7)



(8)

The second reaction is simply an identity reaction and so will not affect the products, but the first reaction reduces the concentration of (7) and in doing so also reduces the chance of forming the bibenzyls (1) and (2). Since (7) and (8) are formed by the reaction of the carbene (5) with bromodurene the chance of their immediate

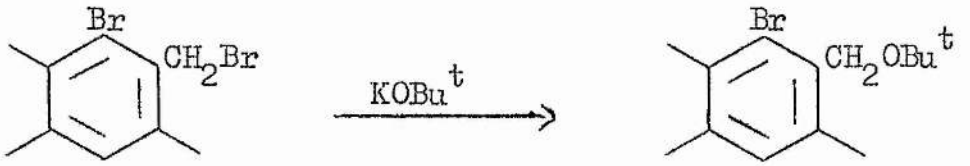


(1) (2) (3)

dimerisation to give the monobromobibenzyl (2) is probably fairly high. If they do not dimerise immediately then (7) may react by radical transfer and be destroyed. As the concentration of durene increases, the chances of the carbene (5) reacting with durene instead of bromodurene become greater, thus increasing the likelihood of formation of the bibenzyl (1). This agrees qualitatively with the observed result, that the concentration of (1) relative

to (2) and (3) increases markedly while the ratio of (2) : (3) changes far less.

A common method for obtaining evidence for a multistep reaction scheme is by adding one of the intermediate compounds to test whether this affects the formation of products. In this case the intermediate benzyl bromide (11) of Scheme III provides a possible means for determining whether the radical or anionic mechanism applies. It can be argued that if the benzyl bromide (11) is formed, it should react with potassium t-butoxide to form the aryl t-butyl ether (14):

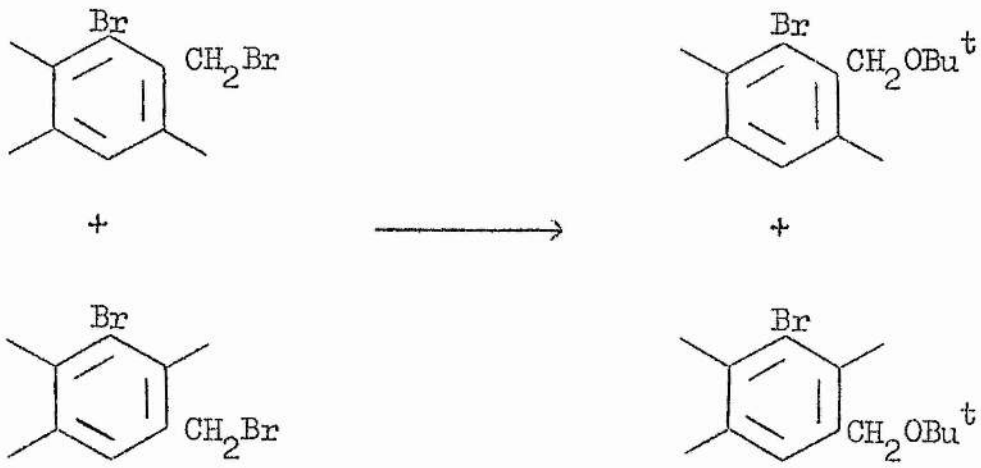


(11) (14)

On the other hand, under the conditions of the reaction this compound might decompose, thus accounting for the fact that it was not isolated in reactions of bromodurene with potassium t-butoxide.

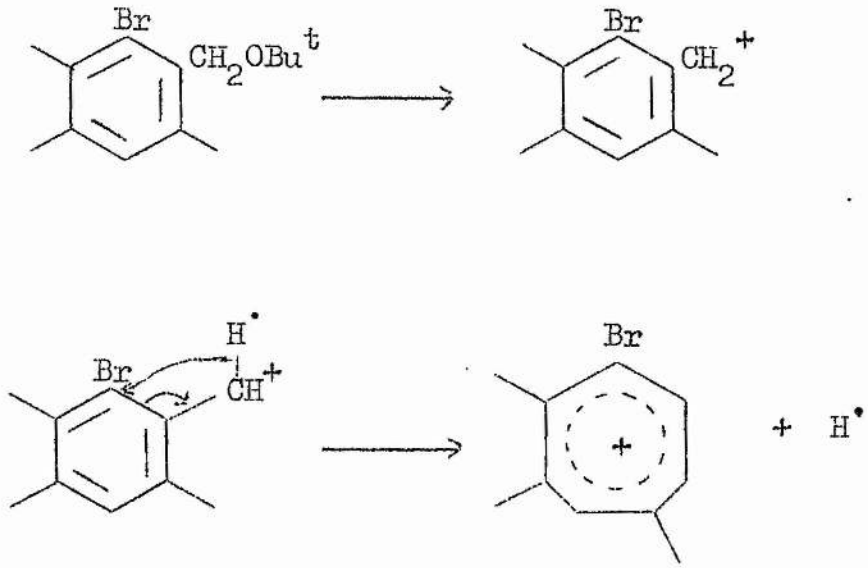
When bromodurene and potassium t-butoxide were allowed to react in the presence of the benzyl bromide (11) the t-butyl ether, about 11 m/100 m. of benzyl bromide, was isolated. This was in fact a mixture of the isomers 2-bromo-3,4,6-trimethylbenzyl t-butyl ether and 3-bromo-2,4,5-trimethylbenzyl t-butyl ether corresponding to the

isomeric benzyl bromides used.



The mixture of ethers was identified from its n.m.r. spectrum which showed two singlets (τ 3.01 and 3.20) for the aromatic proton. due to the two possible isomers. Two singlets (τ 5.47 and 5.71), corresponding to two protons in all, were attributed to the benzyl group, again the position of the group in the two isomers leading to slightly different chemical shifts. The three aromatic methyl groups gave rise to complex absorption (τ 7.50-7.82) while the singlet absorption at τ 8.73 was typical of t-butyl ether groups.

The most abundant ions in the mass spectrum appear at m/e 210, 212 and 211,213, their intensities indicating that these ions contain bromine. The ion at m/e 211,213 can be attributed to loss of C_4H_9O, while the ion at m/e 210,212 is the tropylium ion, possibly formed as shown:



The molecular ion, at m/e 284,286, is of low abundance only, and other ions of low abundance can be attributed to break-up of the tropylium ion.

This result appears to rule out Scheme III as a possible mechanism for the reaction of bromodurene with base. An examination of the other products of the reaction gives further information pertaining to the correct mechanism.

The results of this reaction and of one carried out under the same conditions, to which the benzyl bromide was not added, are summarised in Table I.

The increase in the yield of dibromohexamethylbibenzyl must be due to reaction of the added benzyl bromide with the benzyl anion formed in the initial reaction of butoxide ion with bromodurene.

TABLE I: Reaction of Bromodurene with Potassium t-Butoxide

Product	Yield m/100 m. with $ArCH_2Br$	Yield m/100 m. without $ArCH_2Br$
Durene	24.6	21.7
Hexamethylbibenzyl	0.4	2.7
Bromohexamethylbibenzyl	4.8	10.7
Dibromohexamethylbibenzyl	7.6	5.4

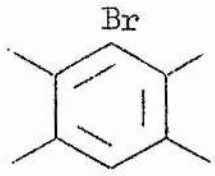
If durene arises from the further reaction of this anion then one would expect the yield of durene to be decreased with added benzyl bromide, since the anion is removed by the benzyl bromide. However the yield of durene is about the same whether the benzyl bromide is there or not, which, on this argument, is more closely in agreement with Scheme II than with Schemes I or III. The yields of hexamethylbibenzyl and bromohexamethylbibenzyl are decreased by adding benzyl bromide, suggesting that they do arise by reactions of the benzyl anions. This is satisfied by all three schemes, but it does support the supposition that removal of the benzyl anion decreases the yield of products formed from it.

The evidence on mechanism so far is conflicting, but on balance it appears that a combination of Schemes I and II provides the most satisfactory explanation: that is, that genesis of bibenzyls occurs via the unsaturated carbene, and that of durene by base debromination, although the identity of the debrominating reagent is uncertain.

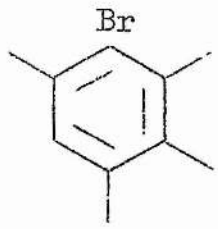
Experiments involving other 2,6-dimethylaryl halides, described below, go some way to supporting this rationale.

2. Reactions of Other 2,6-Dimethylaryl Halides with Potassium t-Butoxide

The reaction of potassium t-butoxide with a number of 2,6-dimethylaryl halides containing different numbers and arrangements of methyl substituents has been studied, as have the behaviour of chloro- and iododurene towards the same base. The results of these experiments are summarised in Table II. With the exception of chlorodurene, the yield of the dehalogenated polymethylbenzene is about the same in all cases; however the yields of higher-boiling compounds appear to be very dependent on the number of methyl groups in the ring. This difference is due to the change in the number of methyl groups rather than to their position, since bromodurene (15) and bromoisodurene (16) give a very similar range of products. Also one would expect to find similarities between bromodurene and bromo-m-xylene, and between bromoisodurene



(15)



(16)

TABLE III: Reactions of 2,6-Dimethylaryl Halides with Potassium t-Butoxide

Substrate	Yields m/100 m.			
	Poly-methyl-benzene	Bibenzyl	Halo-bibenzyl	Dihalo-bibenzyl
bromopentamethylbenzene	32.7	4.65	20.5	11.9
bromoisodurene	32.4	1.65	5.7	4.5
bromodurene *	35	←	10	→
iododurene	35.5	1.0	6.8	4.9
chlorodurene **	25.3	0.2	1.5	0.9
bromomesitylene **	32.8	0.2 ‡	1.8 ‡	1.45
bromoxylene **	36.5	none	isolated	

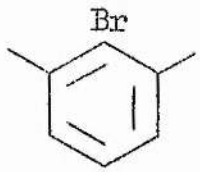
* Results obtained by Dr. Sharp.

** Methylbromoisopentylbenzenes were isolated in these reactions; from bromoxylene 11.0 m/100 m., chlorodurene 5.6 m/100 m.

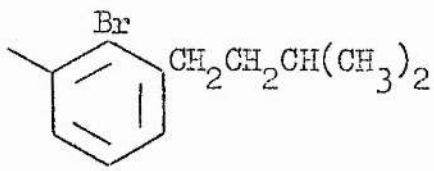
‡ Isomeric diphenylmethanes were also isolated in very low yield.

and bromomesitylene if position of substituents had any substantial effect on the properties.

(a) Bromo-m-xylene.



This compound gives a similar yield, 36.5 m/100 m., of the debrominated compound, xylene, as bromodurene does of durene, but the differences in the higher boiling compounds are considerable. The bibenzyl dimers are present in very low yield indeed, if at all, and the only other product isolated, besides xylene, was the bromomethylisopentylbenzene (17), 11 m/100 m.

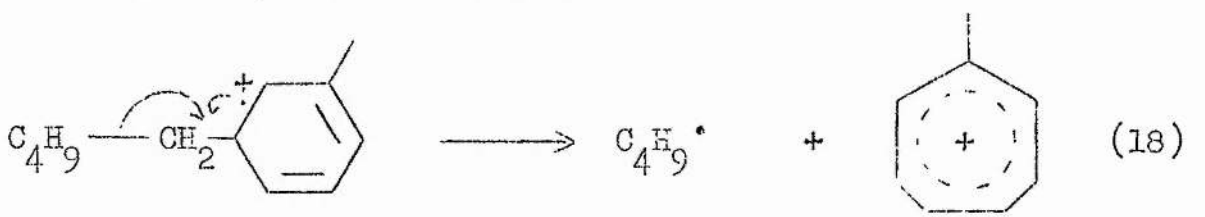


(17)

This compound was identified from its n.m.r. and mass spectra as follows. The three aromatic protons appear as a singlet at τ 3.04, the methyl group attached to the benzene ring gives rise to another singlet at τ 7.63 while the two methyl groups of the

isopentyl chain give rise to a doublet at τ 9.03 with a coupling constant of 5.5 c/s. The two methylene groups of the isopentyl chain give rise to an A_2X_2 system centred on τ 7.87. The single proton of the isopentyl group is superimposed on the up-field half of this system.

The mass spectrum has two parent ions of almost equal abundance at m/e 240 and 242 indicating the presence of bromine in the molecule. Other ions containing bromine correspond to the loss of CH_3, C_3H_7, C_4H_9 and C_5H_{11}. The most abundant ion, at m/e 105, corresponds to the ion $C_8H_9^+$ which probably has the structure shown (18). This would be formed by benzylic cleavage[106] from the ion m/e 161 formed by loss of bromine.



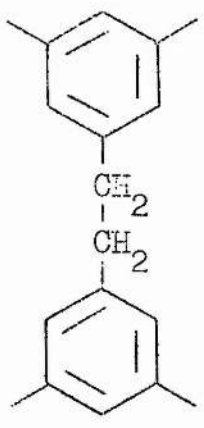
(18)

The structure of this compound was confirmed by preparation of an authentic sample.

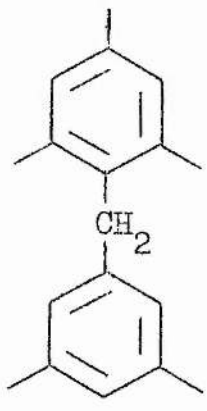
The source of this compound is somewhat obscure. A possible explanation is that it is formed by addition of a benzyl anion or radical to isobutene, which might arise by dehydration of t-butanol which will be present in the reaction mixture.

(b) Bromomesitylene. A compound containing an isopentyl side chain was also isolated in the reaction of bromomesitylene with potassium t-butoxide. It was identified by its n.m.r. spectrum, which resembled that of 2-bromo-3-methylisopentylbenzene closely. Unfortunately insufficient material was available to obtain an accurate analysis, but g.l.c. data suggested that less than 2 m/100 m. was present.

The bibenzyl dimers were formed in this reaction, but in very much lower yields than in the case of bromodurene. In addition, the sample containing 3,3',5,5'-tetramethylbibenzyl (19) isolated by preparative g.l.c., was found to be a mixture of this compound, with 2,3',4,5',6-pentamethyldiphenylmethane (20) from the n.m.r. spectrum, which showed an absorption at 6.15τ identical to the methylene absorption of (20).



(19)

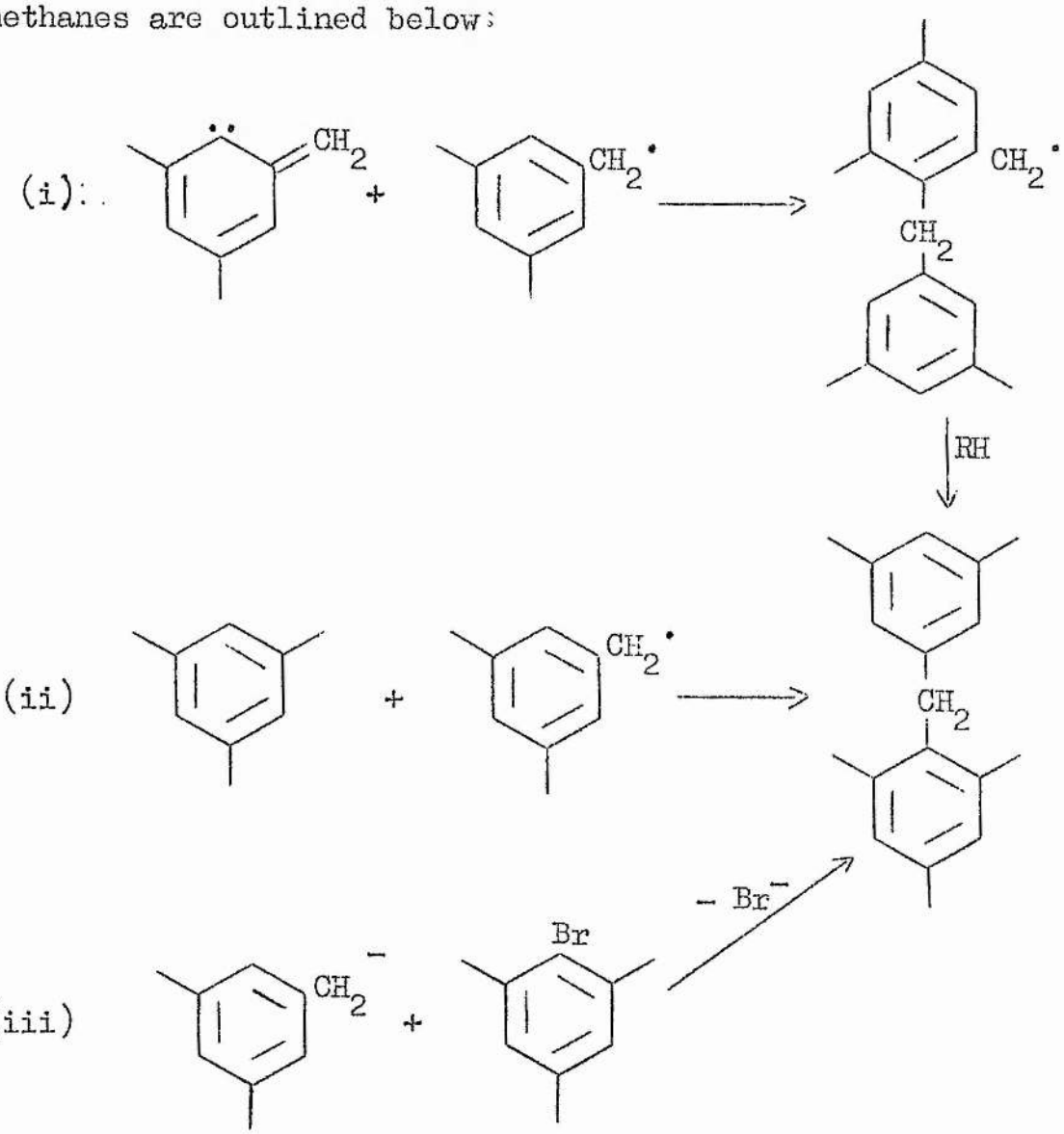


(20)

Absorptions due to the aromatic protons and to the methyl groups

also indicated that the sample contained a mixture of these two compounds. A sample of bromo-2,3',4,5',6-pentamethyldiphenylmethane was also isolated and identified by its n.m.r. spectrum, which consisted of a singlet (τ 3.21) due to the aromatic protons and a singlet (τ 6.10) due to the methylene protons. The methyl groups gave rise to a complex absorption at τ 7.55-7.94.

Three possible mechanisms for the formation of these diphenylmethanes are outlined below:



Direct nucleophilic displacement, reaction (iii), on this deactivated aromatic ring would appear to be very unlikely. Furthermore it might also be expected to lead to the formation of diphenylmethanes with the other compounds studied. This is certainly not observed with the more highly substituted aryl halides where considerable amounts of bibenzyls only were isolated.

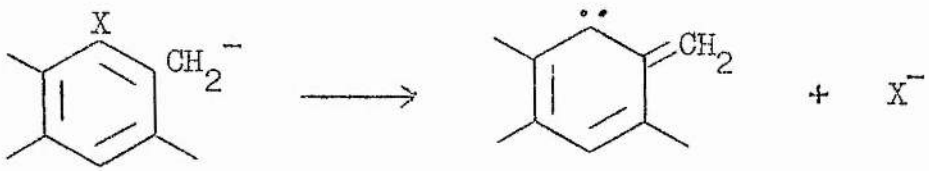
As was stated in the Introduction, Williams[80] finds that phenyl radicals are too reactive to combine with other radicals, as suggested in reaction (i). It is possible that in this case the phenyl radical may be protected by the presence of methyl groups adjacent to the radical site, but again one would expect the same reaction to occur with bromodurene and bromoisodurene.

On the whole, reaction (ii) seems to provide the least unlikely explanation for the formation of this product. Although benzyl radicals do not appear to substitute in aromatic rings under normal conditions,[80] it is possible that, at the high temperature at which these reactions were carried out, they are more reactive. Radical transfer reactions, for example do occur to some extent at high temperatures.[79]

The chances of such substitutions occurring are increased with bromomesitylene over bromodurene since the number of sites available for ring substitution are increased. On this argument bromo-m-xylene

should give diphenylmethanes also. It is possible that the small yield of high boiling products obtained did include diphenylmethanes.

(c) Chlorodurene. Chlorodurene is the only compound studied which gives a decreased yield of the polymethylbenzene product. This is in keeping with the greater electronegativity of chlorine which would make it less susceptible to nucleophilic attack.[9,49] The yield of bibenzyls is also very much reduced in the case of chlorodurene. This can be explained by the relative rates of loss of halide ions from the system:



The relative rates of loss of halogen from o-halogenophenyl anions in the formation of benzynes are Br > Cl > F,[9] and it seems reasonable that this series should also apply here.

The formation of the isopentyl compound analogous to 2-bromo-3-methylisopentylbenzene suggests that it arises from the benzyl anion rather than the radical, providing an alternative course of reaction for the anion in systems where it is less likely to decompose to the carbene.

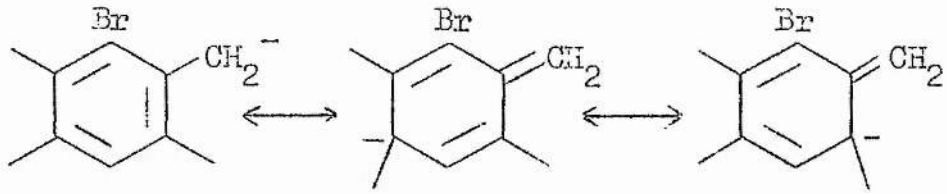
(d) Iododurene. It might be expected that, just as chlorodurene is less reactive than bromodurene towards base, iododurene would be more reactive. In fact it is found that iododurene and bromodurene give almost identical yields of products. However Hoffmann[9] gives the following relative rates of halide loss from o-halogenophenyl anions:- I = 100, Br = 40, Cl < 2, and figures given by Ingold[107] for relative leaving abilities of halides in SN1 and E1 processes, parallel this; that is iodide 1.5-4.5 times faster than bromide, bromide 25-60 times faster than chloride. One would, therefore, expect very much smaller differences between iododurene and bromodurene than between bromodurene and chlorodurene, and these might well not be noticeable in this system. If one takes the least favourable of Ingold's figures, that is iodide 4.5 times faster than bromide and bromide 25 times faster than chloride, this leads to an expected increase of approximately 1.5 m/100 m. in the total yield of bibenzyls from iododurene over bromodurene, on the basis of the change in yield between chlorodurene and bromodurene. This is, in fact, observed.

(e) Bromoisodurene. When the reactions of bromodurene and bromomesitylene with potassium t-butoxide were compared, it seemed possible that the position of the substituent methyl groups might affect product formation in some way. However, the composition of

high-boiling products obtained from reactions of bromodurene and bromoisodurene are so similar that the variation in yield of high-boiling products from reactions of different polymethylaryl halides must be a function of the number of methyl groups rather than of their position.

(f) Bromopentamethylbenzene. The latter observation is borne out by the fact that the system bromopentamethylbenzene/potassium t-butoxide gives an increase in the yield of bibenzyl products over bromodurene and potassium t-butoxide. In the series bromomesitylene, bromodurene, bromopentamethylbenzene, the introduction of one methyl group seems to be equivalent to a three- to fourfold increase in the yield of bibenzyl dimers. In other words the introduction of a methyl group favours the formation of the triplet carbene, (5), postulated in Schemes I and II.

This phenomenon can be explained as follows. Since methyl groups are electron-donating they would tend to favour the loss of halide ion from the benzyl anion. Such an effect is observed in benzyne formation, where alkyl groups increase the rate of loss of halide ion from o-halogenophenyl anions by destabilizing the negative charge.[9] The negative charge on the benzyl anion can also be delocalised in the aromatic ring and is subject to the same destabilization:

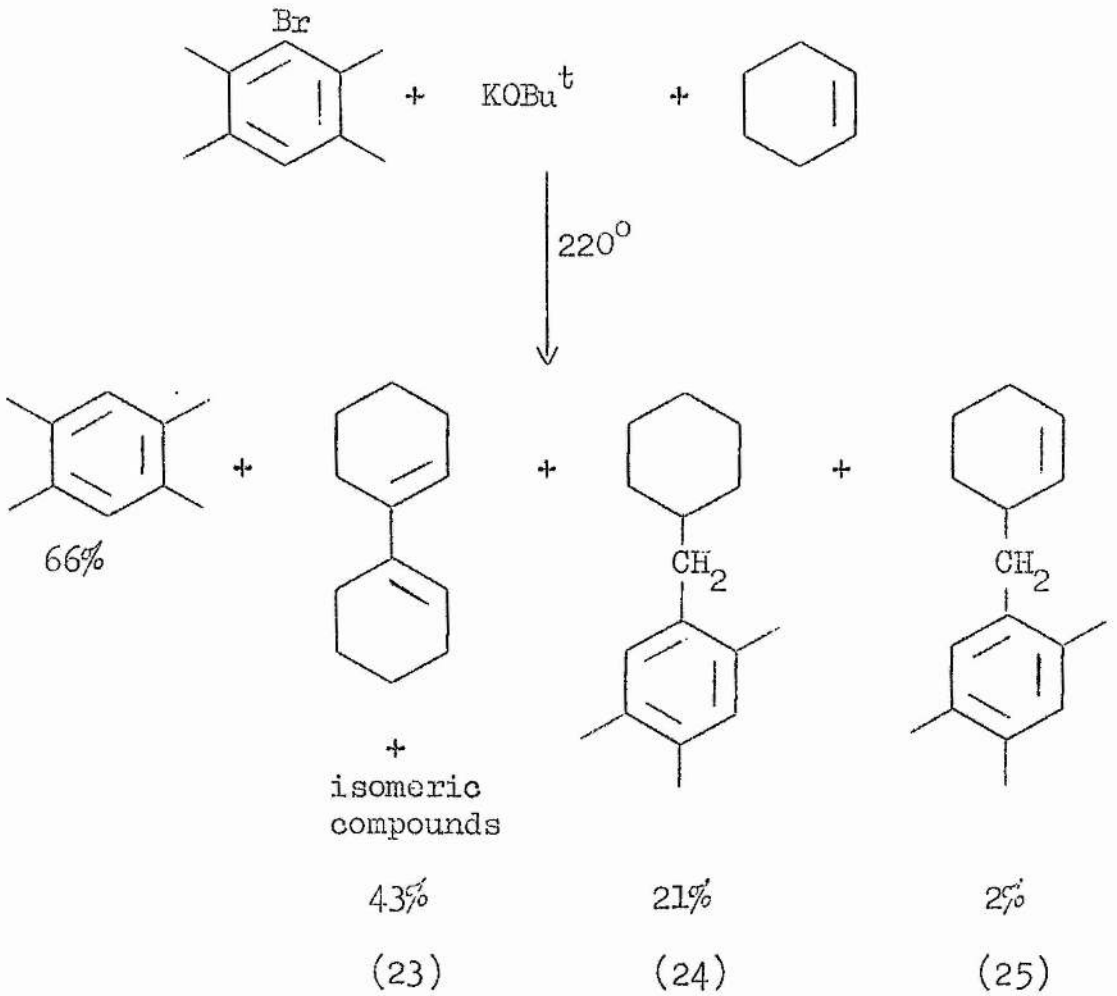


Although the results of the experiments discussed above do not, on their own, offer any clear indication as to mechanism, they are generally consistent with the combination of Schemes I and II suggested at the end of Section 1, page 114.

3. Reactions of 2,6-Dimethylaryl Halides with Potassium t-Butoxide in Cyclohexene

Bifunctional intermediates such as 1,3-dipoles frequently form cyclic addition products with olefins.[108] However Closs and his co-workers[103] found that the triplet carbene, diradical, intermediate generated in the photolysis of 3H-indazoles did not form cyclic addition products with simple olefins, and perhaps it is not surprising to find that such addition products were apparently not formed when bromodurene and potassium t-butoxide were allowed to react in the presence of cyclohexene.[83]

The results of this reaction are outlined below, and results with this and other 2,6-dimethylaryl halides are summarised in Table III.



In these reactions yields are calculated on aryl halide and not on base, since this was in excess, so that a direct correlation with results of experiments discussed in Sections 1 and 2 is not really possible. However the data from these reactions can be explained satisfactorily on the basis of the radical reactions outlined in Schemes I and II. Routes to the observed products are suggested in Scheme IV.

Scheme IV

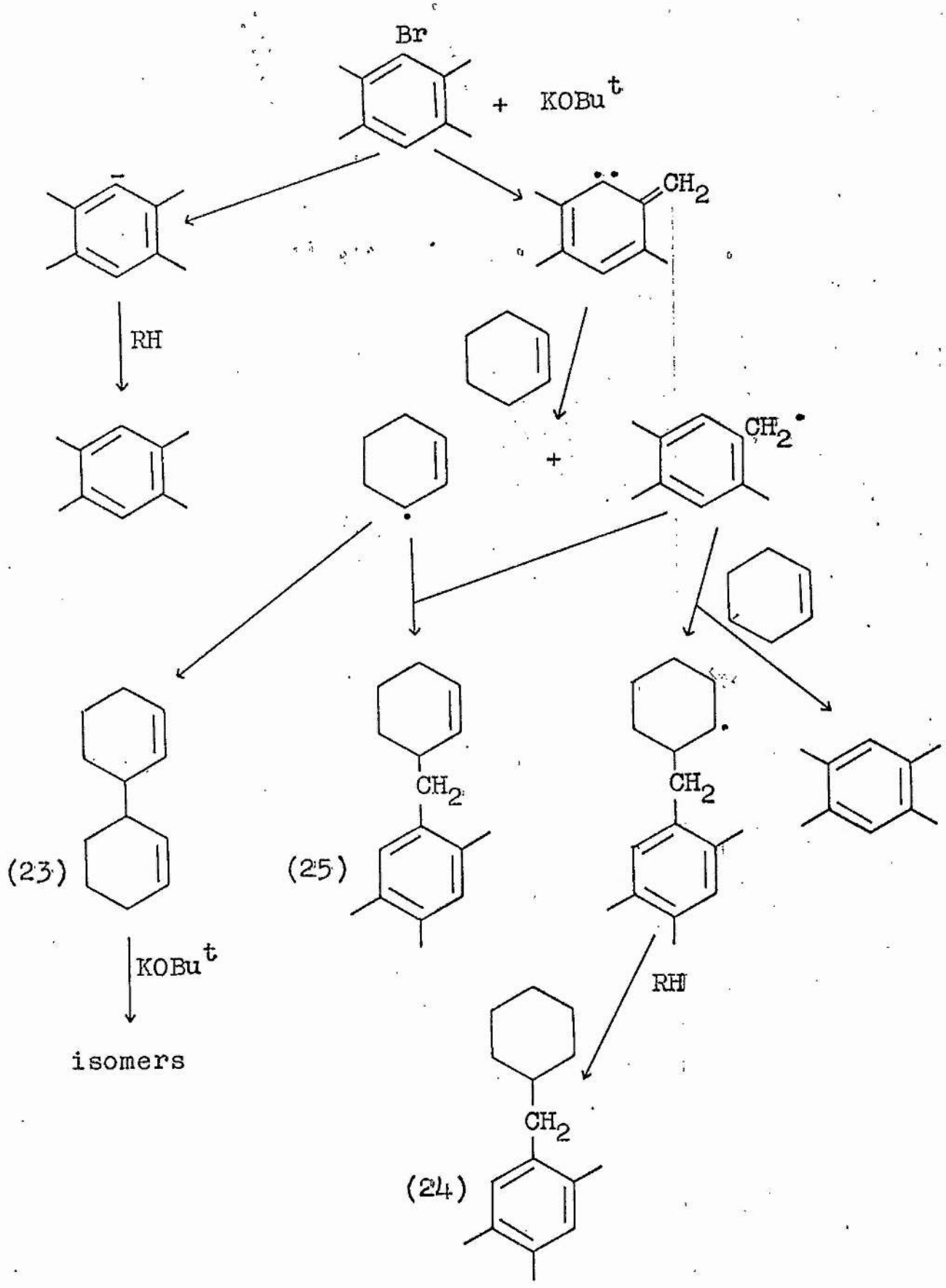


TABLE III: Reaction of 2,6-Dimethylaryl Halides with Potassium t-Butoxide in the Presence of Cyclohexene

Substrate	Yields m/100 m. of substrate			
	Poly-methyl-benzene	Bicyclo-hexenyl	Aryl-cyclo-hexyl-methane	Aryl-cyclo-hexenyl-methane
bromopentamethyl-benzene *	54.0	43.8	9.1	12.0
[bromodurene	66.0	43.0	21.0	2.0]
chlorodurene	19.8	23.1	4.5	1.2
bromomesitylene	60.5	22.5	none isolated	

(* octamethylbibenzyl 1.5 m/100 m. was also obtained in this reaction.)

Instead of forming an adduct, cyclohexene acts as a hydrogen donor, apparently to the exclusion of bromodurene, in view of the absence of bromine in any of the high-boiling radical-formed products. This is reasonable since cyclohexene is in very great excess, and since it is a very much better hydrogen donor towards phenyl radicals, for example, than toluene and its derivatives.[70] Subsequently the cyclohexenyl radicals so obtained can dimerise to form bicyclohexenyl (23), or combine with benzyl radicals to give the (trimethylphenyl)cyclohexenylmethane (25). Alternatively the benzyl radical can add to the double bond of cyclohexene to give, after hydrogen abstraction, (trimethylphenyl)cyclohexylmethane (24).

With benzyl radicals addition and combination are alternatives, and the relative rates of the two reactions reflect the stability of the radical involved. Thus the ratio of cyclohexylmethane to cyclohexenylmethane found in the product gives an indication of the stability of the benzyl radical involved. On this assumption, the results obtained here are in agreement with the greater stability of the radical derived from pentamethylbenzene over that derived from durene, which might be expected in view of the greater number of substituents.[109] With the former, combination is slightly favoured over addition, and dimerisation of benzyl radicals also occurs to some extent, while with the latter addition is very much the preferred reaction.

If the assumption that the ratio of cyclohexylmethane (24) to cyclohexenylmethane (25) reflects the stability of the benzyl radicals involved then the same ratio should be obtained with chlorodurene as with bromodurene, since the same radical is involved. Although (24) is formed to a greater extent in both cases, the size of this ratio is not the same. It is possible that the small yields obtained from chlorodurene led to inaccuracies in their measurement. Again the low yields of products obtained from chlorodurene indicate the lower reactivity of chlorine, both towards nucleophilic attack and in radical-formation.

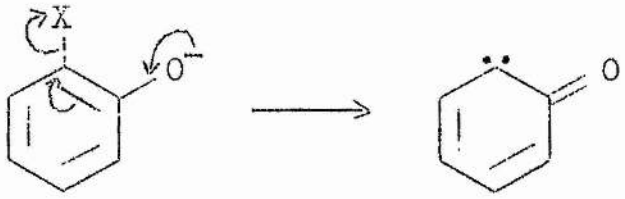
If it is assumed that dimerisation of cyclohexenyl radicals

is the major source of bicyclohexenyl then the yield of this indicates the degree of radical-formation. The yields obtained with bromomesitylene agree with the data presented in Section 2 that it is as reactive as bromodurene towards nucleophilic attack, but much less reactive in radical-formation.

The results of the experiments discussed in these three sections suggest the possibility of participation of a triplet carbene intermediate in the reaction of 2,6-dimethylaryl halides with strong base. The possibility of extending this mechanism to other systems led to an investigation of the thermal decomposition of o-halophenol salts.

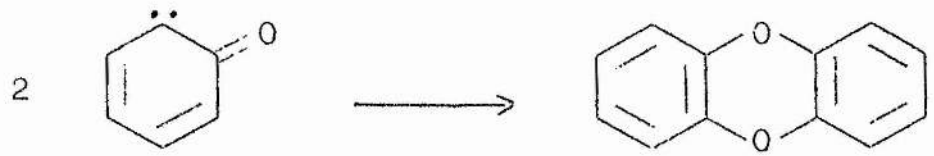
4. The Thermal Decompositions of o-Halophenol Salts

The anions of o-halophenol salts are similar to the o-halobenzyl anions discussed previously, and it is possible to write a similar decomposition to a carbene:



It is interesting, therefore, to find that the principal

product, which has been isolated [52,53,61] from reactions of this type of system, is diphenylene dioxide (26) and its derivatives:



(26)

In addition the polyphenylene oxides also obtained could arise by radical chain processes for which the carbene intermediate might act as initiator.

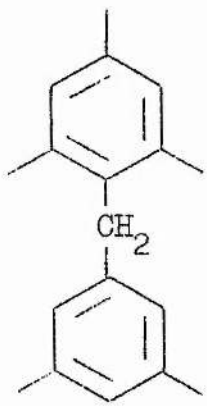
Since the participation of radical intermediates, postulated in the reaction of bromodurene with potassium t-butoxide, was deduced from their reaction with the methyl side-chains of aromatic compounds, it seemed reasonable to attempt to detect radical intermediates in the thermal decomposition of sodium o-halophenates by conducting the decompositions in suitable methylbenzenes.

The decomposition of o-bromophenate in mesitylene gave, however, diphenylene dioxide as the sole product, and the solvent was not attacked to any detectable extent.

Attempts to form cycloaddition products of the carbene with trans-stilbene, as has been done by Huisgen and his co-workers, [108,110] were also unsuccessful. Again the sole product was diphenylene

dioxide.

However the thermal decomposition of sodium pentachlorophenate in mesitylene did involve attack on solvent to a considerable extent. The n.m.r. and mass spectra indicated quite clearly that this was not 3,3',5,5'-tetramethylbibenzyl which would be obtained from radical intermediates, but the isomeric diphenylmethane (29).

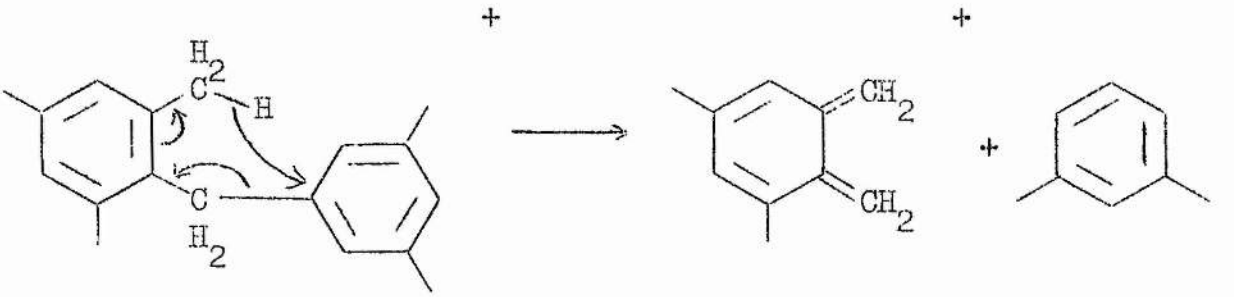


(29)

Instead of a singlet absorption at τ 7.15, due to the ethane protons of the bibenzyl, a singlet at τ 6.15 corresponding to two protons only was observed. This was attributed to the methylene group of (29); the aromatic protons gave rise to a complex absorption between τ 3.20 and τ 3.60, and the methyl groups to a complex absorption at τ 7.65-7.85.

The mass spectrum was identical to that reported by Meyerson, Drews and Fields[102] for (29), showing, in addition to abundant even-electron ions at m/e 238 and 223 which are the molecular ion and

the ion formed from it by loss of a methyl group, an abundant odd-electron ion at m/e 132. They accounted for this ion by the rearrangement shown:



2,3',4,5',6-Pentamethyldiphenylmethane (29) was obtained from the thermal decomposition of sodium pentachlorophenate in mesitylene in a yield of 30 m/100 m. of phenate. In addition 2,3,5,6-tetrachlorophenol (11 m/100 m) was isolated, but no octachlorodiphenylene dioxide was detected. However octachlorodiphenylene dioxide, 0.74 m/100 m., was formed when the decomposition was carried out in t-butylbenzene under the same conditions. This solvent was not attacked.

The results of carrying out the thermal decomposition in a range of methylated solvents are summarised in Table IV. The diphenylmethanes were identified from their n.m.r. spectra in conjunction with either their mass spectra or elemental analyses. Authentic samples of the tetrachlorophenols were available for comparison, but the trichlorophenol was identified from its n.m.r.

TABLE IV: Thermal Decomposition of Sodium Pentachlorophenate in Various Solvents

Solvent	Yields m/100 m.			
	Diphenyl-methane	Trichloro-phenol	Tetrachlorophenols: 2,3,5,6-	2,3,4,5-
p-xylene	36.8		8.0	10.4
p-xylene *	18.6	7.9	2.80	
p-xylene and t-butylbenzene	25.5 ** 5.2 ‡	10.0	8.5	3.5
mesitylene	30.3		11.0	
durene	24.5	7.0	3.7	2.4

* reaction was carried out in a glass tube.

** 2,4',5-trimethyldiphenylmethane.

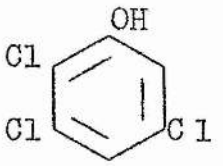
‡ t-butyl-4-methyldiphenylmethane.

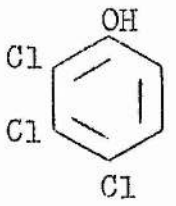
and mass spectra as follows:

The most abundant ion was the molecular ion at m/e 196-202, the intensities of the ions indicating that it contained three chlorine atoms. An ion at m/e 160 containing two chlorine atoms was formed by loss of HCl and an ion at m/e 132 also containing two chlorine atoms was formed by loss of CO from this ion. An ion of low abundance at m/e 125 represents loss of HCl_2 from the molecular ion and this is accompanied by an ion at m/e 97 which is accounted for by loss of CO from it.

The aromatic absorption of the n.m.r. spectrum took the form

of two doublets (τ 2.95 and 3.05) both with a splitting constant of 2.4 c/s. Since the two aromatic protons have different chemical shifts the chlorine atoms must be arranged 2,3,5 or 2,3,4 as shown, since in any other isomer the protons would have nearly identical chemical shifts:



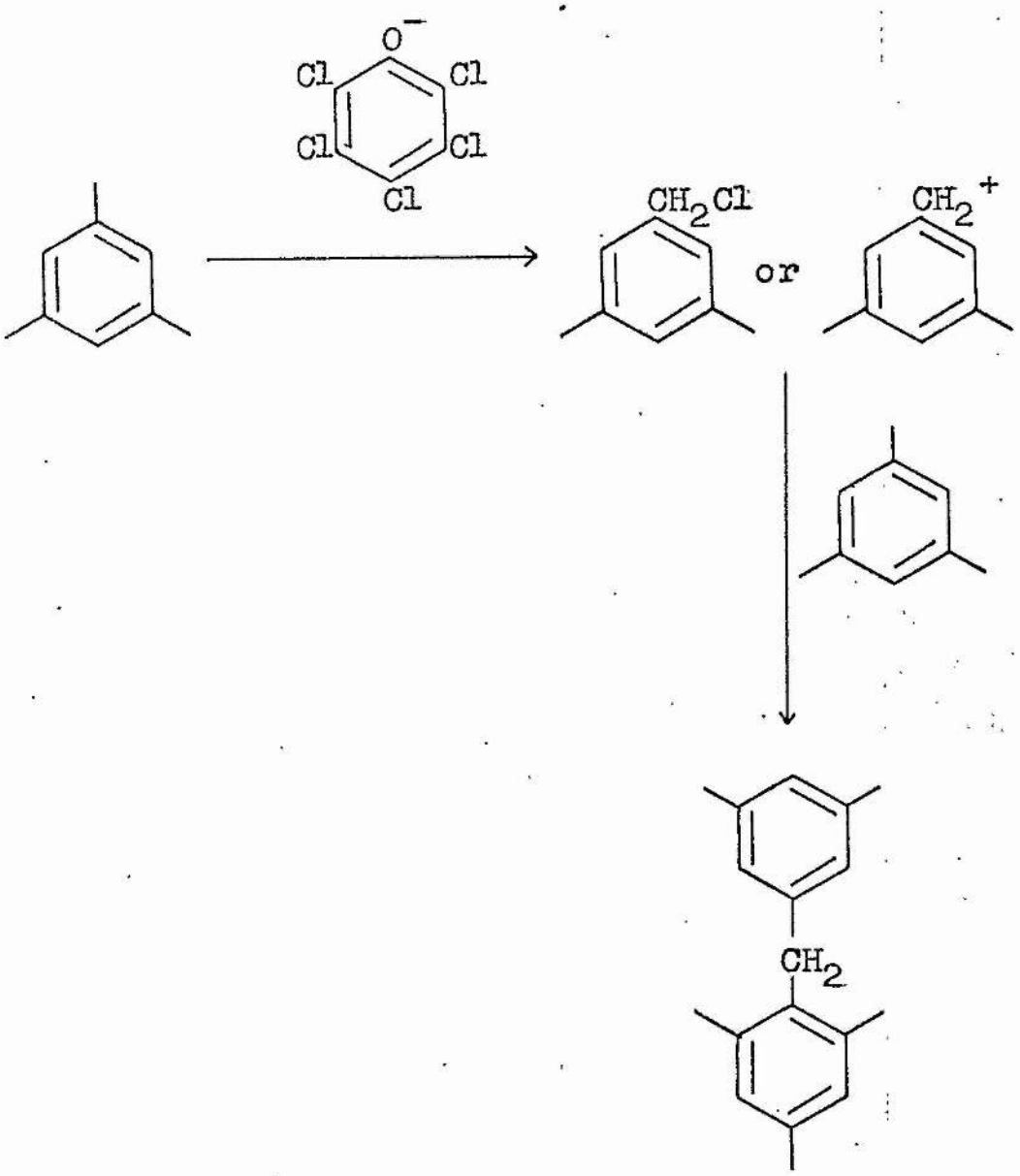


The size of the coupling constant (2.4 c/s) indicates that the compound is the 2,3,5-trichloro isomer with the protons meta to each other. The 2,3,4-trichloro isomer would have a much higher coupling constant between the protons.

Other acid products of the reaction could not be isolated or identified, but g.l.c. examination showed that 2,3,4,6-tetrachlorophenol was not formed. No other acid products with similar retention times to the trichlorophenol were formed to any great extent, and it seems possible that chlorine was not lost from the meta position of the pentachlorophenate anion.

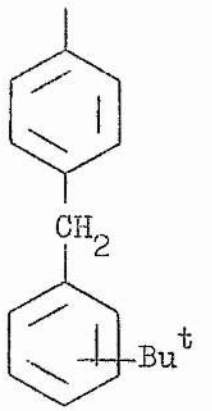
Clearly the diphenylmethane are not formed by a carbene intermediate analogous to that postulated in the reaction of bromodurene with base, since this would be expected to give benzyl radicals. The latter would certainly not give diphenylmethane as

Scheme V



the major product.

The decomposition of sodium pentachlorophenate carried out in a mixture of p-xylene and t-butylbenzene gives the cross-product (30), 5.2 m/100 m.,



(30)

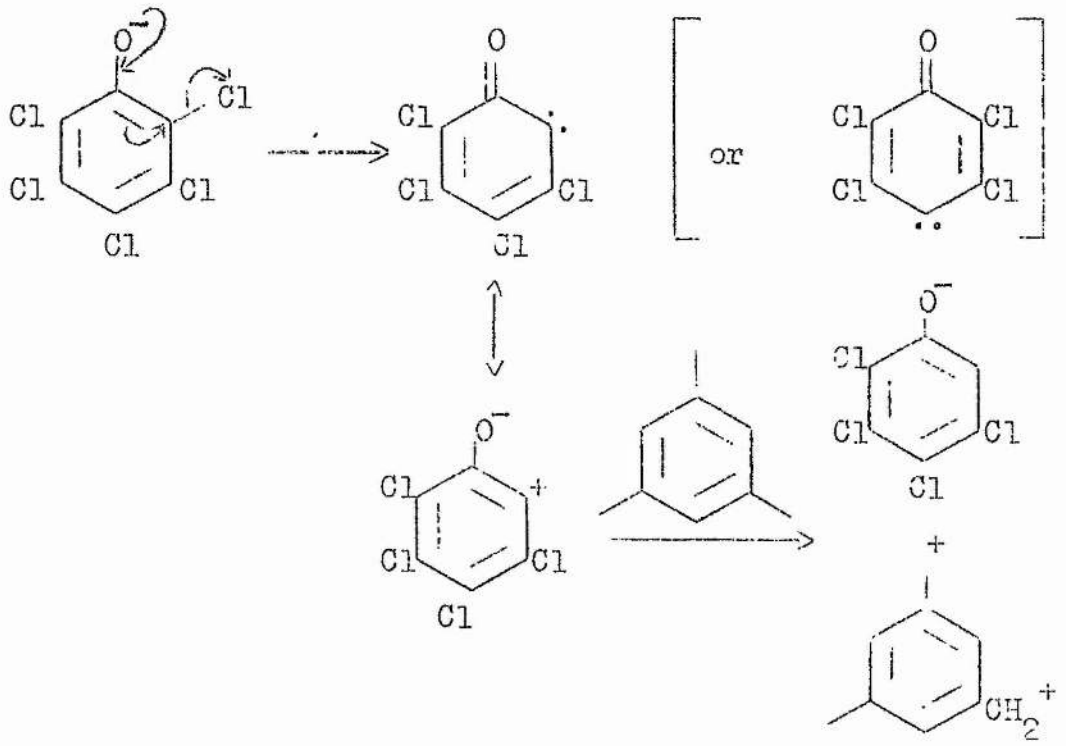
in addition to 4,4'-dimethyldiphenylmethane. The formation of this product suggests a two-step mechanism involving initial attack on the methylated aromatic compound to give an intermediate which will substitute on an aromatic ring to give the diphenylmethanes.

Possible intermediates are a benzyl carbonium ion or a benzyl chloride. This is outlined in Scheme V.

A satisfactory mechanism must explain the following observations. The formation of diphenylmethane is probably a function of the large number of chlorine atoms in the pentachlorophenate anion since no reaction is observed with o-bromophenate ions. Loss of chlorine appears to be assisted by the presence of methylbenzenes. Thus, under the same conditions, about 40 m/100 m. of chloride ion

was displaced when sodium pentachlorophenate was decomposed in t-butylbenzene, as opposed to about 130 m/100 m. in methylbenzene solvents. Finally chlorine appears to be lost from positions ortho and para to the phenate group only. The mechanisms which follow satisfy some, but not all, of these points.

A mechanism leading to formation of a benzyl carbonium ion is outlined in Scheme VI:

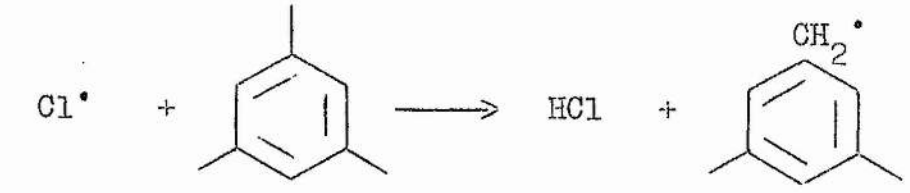


Scheme VI

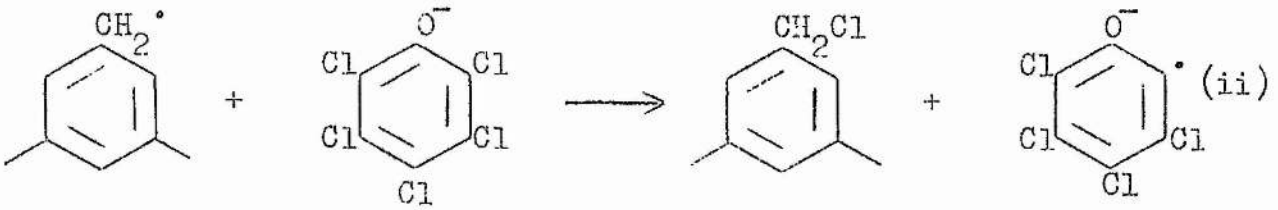
Although this scheme explains the loss of chlorine from ortho and para positions only, it is unsatisfactory in other ways. It does

not, for example, explain why the reaction is not observed with o-bromophenate salts; in fact one might expect the carbene intermediate to be formed more readily from the o-bromophenate anion.

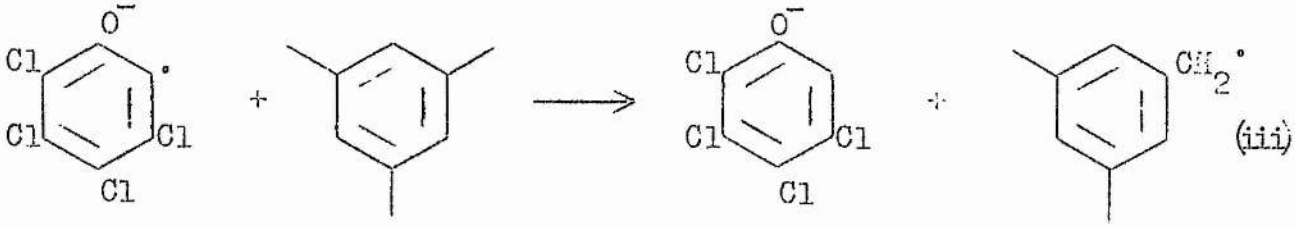
Since Kulka[63] suggests a radical mechanism for the formation of diphenylene dioxide, it is possible that some kind of radical chlorination of the methylbenzene is involved here. Such a mechanism is formulated below. A chlorine atom is used as initiator in step (i) since Kulka suggests that this radical is formed in the formation of diphenylene dioxide.



(i)



(ii)

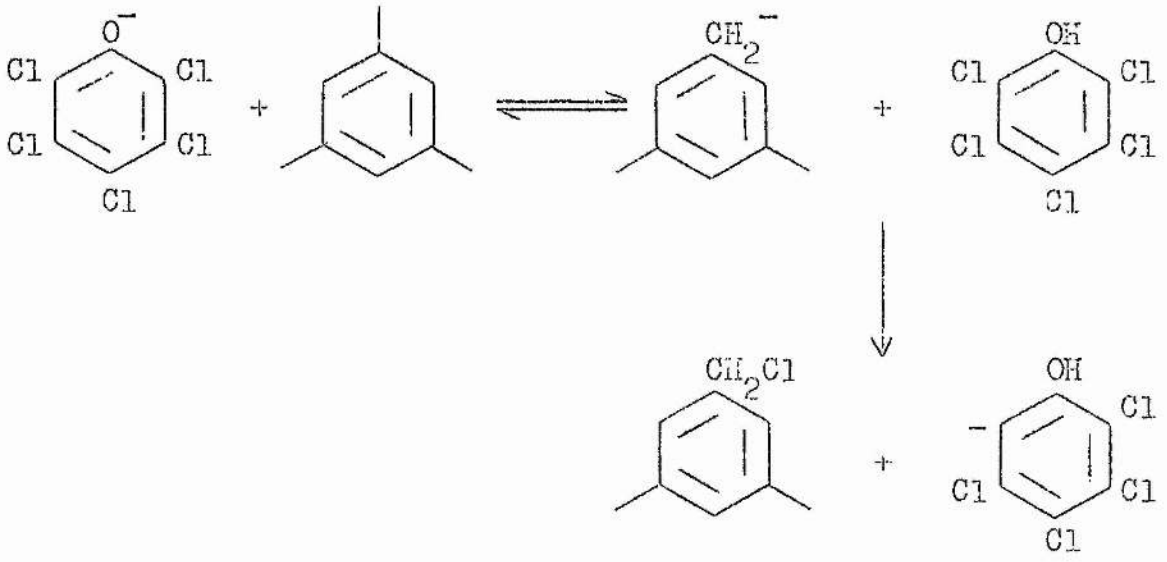


(iii)

This mechanism explains the increased loss of chlorine in the

presence of methylbenzenes, but it does not explain the preferential loss of chlorine from the ortho and para positions. Although steric influences would be expected to increase the lability of the chlorine in sodium pentachlorophenate, it is surprising that no attack on solvent is detected with sodium o-bromophenate, if this mechanism is correct. Finally the fact that very little, if any, bibenzyl is formed is surprising, although Russell and Brown,[111] for example, do not report the formation of bibenzyls in the photochlorination of toluene with chlorine.

A mechanism involving nucleophilic attack on chlorine can also be formulated.



Again this is not wholly satisfactory. It fails to explain, for example, the lack of attack on meta chlorine.

On the whole the formation of benzyl chloride rather than a carbonium ion as an intermediate seems to provide slightly less unsatisfactory mechanisms, but more experimental evidence is required before a clear picture can be obtained. None of the evidence presented gives any reason to suggest the participation of a triplet carbene similar to that postulated in the reaction of bromodurene with base.

5. Conclusions

The experiments, involving 2,6-dimethylaryl halides and strong bases discussed in this thesis, indicate the formation of a bifunctional intermediate differing from benzyne intermediates in that it has a triplet structure, but formed by a similar set of reactions.

Most of the evidence obtained from these experiments is consistent with the suggestion that the polymethylbenzene is formed by direct nucleophilic attack on the halogen by base. Although the fate of the base derived product formed by this attack is obscure, the fact that the yield of polymethylbenzene is dependent only on the nature of the base and the halogen appears to be significant.

The differences in the products obtained from the various 2,6-dimethylaryl halides studied are explained satisfactorily by the mechanism which is outlined in Scheme II (page 106).

On the other hand the attempt to extend this mechanism to the decomposition of o-halophenol salts is not valid. Although the origin of the products formed from sodium pentachlorophenate is uncertain, there is no evidence that a triplet carbene intermediate analogous to that formed by the 2,6-dimethylaryl halides is involved.

It is clear, therefore, that the new reactions described in this thesis, although formally involving relatively simple reactants, are not easily rationalised in terms of classical reactive intermediates.

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